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RUBBER CHEMISTRY AND TECHNOLOGY

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VOLUME IV NUMBER 4

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Secretary-Treasurer.....H. E. Simmons

Vol. IV October, 1931 No. 4

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. Simmons, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman..... E. R. Bridgwater, E. I. du Pont de Nemours & Co.
Vice-Chairman.....L. B. Sebrell, Goodyear Tire & Rubber Co.
Secretary-Treasurer..... H. E. Simmons, University of Akron, Akron, Ohio
Executive Committee.....H. A. Winkelmann, W. N. Jones, H. A. .....Shepard, H. R. Thies, S. M. Cadwell
Sergeant-at-Arms.....E. H. Nahm

General Meeting of September, 1931

The Rubber Division met in the Lafayette Hotel, Buffalo, September 2, 1931, at 9:00 A.M. with an attendance of one hundred seventy-five. Chairman H. A. Winkelmann appointed a nominating Committee consisting of R. P. Dinsmore, *Chairman*, C. W. Bedford, W. A. Gibbons, W. B. Wiegand, J. M. Bierer, and J. N. Street. The following program was then given:

Wednesday

9:00 A.M. H. R. Thies. Scorch Retarders and Scorch-Retarding Materials.
9:20 A.M. W. F. Busse. The Mastication of Rubber—An Oxidation Process.
9:45 A.M. A. R. Kemp, W. S. Bishop, and P. A. Lasselle. Oxidation Studies of Rubber, Gutta-Percha, and Balata Hydrocarbons.
10:05 A.M. C. R. Park and R. B. Maxwell. The Temperature Coefficient of Vulcanization.
10:40 A.M. H. C. Jones and Harlan A. Depew. The Influence of Zinc and Lead on the Rate of Cure of Stocks Accelerated with Tetramethyl Thiuram Monosulfide.
11:00 A.M. J. W. Ayers. The Effect of Oxide of Iron Containing Soluble Ferric Sulfate on Rubber.
11:20 A.M. J. H. Ingmanson, C. W. Scharf, and R. L. Taylor. The Effect of Various Accelerators and Antioxidants on the Electrical Characteristics and Water Absorption of Vulcanized Rubber Insulation.
11:40 A.M. M. F. Acken and Wheeler P. Davey. X-Ray Evidence That Rubber Is a Two-Phase System.
6:00 P.M. Banquet. A. R. Lewis, Charles F. Smith, and A. A. Somerville, Committee.

Thursday

9:00 A.M. J. R. Sheppard and W. J. Clapson. Compression Stress-Strain of Rubber.
9:25 A.M. S. D. Gehman and T. C. Morris. Measurement of the Average Particle Size of Fine Pigments.
9:45 A.M. W. L. Holt. Behavior of Rubber under Repeated Stress.

10:05 A.M. Arthur M. Neal. A Study of Flexing.
R. P. Dinsmore. Report of Physical Testing Committee.
H. L. Trumbull. Report of Papers Committee.
Business Meeting. Election of Officers.

The Division elected the following officers to serve for the next year: E. R. Bridgwater, *Chairman*, L. B. Sebrell, *Vice-Chairman*, H. E. Simmons, *Secretary-Treasurer*, E. H. Nahm, *Sergeant-at-Arms*. *Executive Committee:* H. A. Winkelmann, W. N. Jones, N. A. Shepard, H. E. Theis, S. M. Cadwell.

R. P. Dinsmore reported as chairman of the Physical Testing Committee.

By motion the Division expressed its appreciation of the work of the retiring Chairman, H. A. Winkelmann, and the Executive Committee.

Meeting adjourned.

H. E. SIMMONS, *Secretary-Treasurer*

Minutes of the Newly Elected Executive Committee

The discussion of the Spring meeting at Detroit occupied the major portion of the time. S. M. Cadwell was appointed Chairman of the entertainment committee for that meeting.

It was further agreed that if the meeting was held in February we would reduce the six weeks requirement for receiving papers to four weeks prior to the meeting.

The Executive Committee created a new committee, which in the future will be known as the Permanent Program Committee. This committee will be self-perpetuating, and consists of the Chairman, who will be the Vice-Chairman of the Division, assisted by the Chairman of the Division, the Past-Chairman and the Secretary-Treasurer. It will be the duty of this Committee to look ahead and arrange special programs in the form of symposiums, thus giving time for adequate preparation.

H. E. SIMMONS, *Secretary-Treasurer*

Meeting of the Executive Committee

The Executive Committee met Wednesday to discuss the question of meeting places of the Division for the Spring meeting, considering the fact that the Society meets at New Orleans in the Spring and Denver in the Fall. It was voted by the Executive Committee that the Spring meeting would be held in Detroit in February, 1932.

Report of the Treasurer

Balance in the bank, March 30, 1931 (meeting at Indianapolis)	$1374.49	
Dues and subscriptions since March 30, 1931	353.31	$1727.80
Expenditures:		
Translations	$ 262.72	
Ben Franklin Printing Co.	33.75	
Mack Printing Co.	4.44	
Multigraphing letter (H. A. Winkelmann)	12.20	
Postage, telegrams, office equipment, and expenditures	14.77	
Expenses to Indianapolis for Sec'y-Treas. H. E. Simmons	65.00	
Stenographic services	60.00	
Foreign money order—not negotiable (replaced with P. O. Order)	4.00	456.88
Balance in bank, September 1, 1931 (Buffalo meeting)		$1270.92

Secretary's Report

Total membership of the Division		604
Members	379	
Associate members	116	
Subscriptions	77	
Honorary members	32	
	604	
Members who did not renew membership	38	
Associate members who did not renew membership	24	
Subscriptions not renewed	18	
	80	

H. E. Simmons, *Secretary-Treasurer*

Local Group Activities

Los Angeles Group

June 30, 1931. Address by Charles Lamb (West American Rubber Co.) on "The Romance of the Rubber Industry."

August 1, 1931. Golf tournament, dinner, and social evening.

Institution of the Rubber Industry

The Secretary of the *Institution of the Rubber Industry* has very kindly sent to Rubber Chemistry and Technology an Advance Program of Papers to be presented during the season of 1931–1932.

His kindness in sending this program is greatly appreciated, and aside from the few who may actually be fortunate enough to attend some of the meetings, it will acquaint our members with the excellent programs which are planned by the Institution, and will also aid toward a better understanding and appreciation of the efforts and accomplishments of our colleagues across the Atlantic, which is so much to be desired. It is such coöperation which will bring nearer and nearer in spirit and in mutual accomplishment the rubber chemists and technologists of all lands.

Advance Program of Papers

SESSION 1931–1932

London and District Section

To be read at the First Avenue Hotel, High Holborn, London

1931

July 20 "The Importance of Inter-molecular Forces in Relation to the Physical and Technical Properties of Rubber." Prof. Lothar Hock.

Oct. 12 "The Advantages and Disadvantages of Technical Training for Salesmen in the Rubber Industry." A. E. Osborn.

Nov. 9 Paper by Prof. G. Bruni.
Dec. 14 "The Scientific and Economic Development of the Rubber Plantation Industry." F. D. Ascoli.

1932
Jan. 11 "Testing Antioxidants." H. J. Stern and W. Puffett.
Feb. 8 "The Vibration of Buildings and Possibility of Rubber as a Useful Shock Absorber." H. C. Young.
March 14 "The Transportation and Storage of Goods in the Factory." Colin Macbeth.
April 11 "Moulds and the Moulding of Miscellaneous Rubber Goods." Herbert Rogers.
"Presses and Control Gear for the Rapid Moulding of Miscellaneous Rubber Goods." Frederick Siddall.

Midland Section

1931
Oct. 1 *To be read at the Grand Hotel, Birmingham.* Paper by Alexander Johnston.
Oct. 22 *To be read at the Grand Hotel, Leicester.* "Inner Tubes for Pneumatic Tires." B. W. Dunsby.
Nov. 5 *To be read at the Grand Hotel, Birmingham.* "Costing in the Rubber Industry." G. C. Stone.
Dec. 3 *To be read at the Grand Hotel, Birmingham.* "The Scientific and Economic Development of the Rubber Plantation Industry." F. D. Ascoli.

1932
Jan. 7 *To be read at the Grand Hotel, Birmingham.* "Production Control in the Rubber Factory." W. J. Condon.
Feb. 4 *To be read at the Grand Hotel, Birmingham.* Joint Meeting with the Institution of Automobile Engineers. "The Uses of Rubber in Automobiles." George H. Lanchester.
Feb. 18 *To be read at the Victoria Hotel, Wolverhampton.* "Conveyors in a Rubber Factory." H. Willshaw
March 3 *To be read at the Grand Hotel, Birmingham.* Questions' Night.

West of England Section

To be read (unless otherwise stated) at the George Hotel, Trowbridge

1931
Oct. 7 "Rubber as a Protective Agent." G. H. Beeby.
Nov. 4 "The Simple Chemistry of Rubber Manufacture." S. S. Pickles.
Dec. 2 "The Manufacture of Compounding Ingredients." F. H. Cotton.

1932
Jan. 6 "Sales Methods, Campaigns and Advertising for the Marketing of Rubber Products." F. Webster.
Feb. 3 "Developments of Modern Motor Tire Fabrics." W. Knight and Paper by C. H. Birkitt.
March 2 "Production Control in the Rubber Factory." W. J. Condon.

Manchester and District Section

1931
Oct. 8 *To be read at the Manchester College of Technology.* "General Review of Synthetic Resins." R. Maitland.

Nov. 2 *To be read at the Engineers' Club, Albert Square, Manchester.* "Rubber Roadways." L. Gaisman.

Dec. 7 *To be read at the Engineers' Club, Manchester.* Paper by E. H. Wallace.

1932

Jan 4 *To be read at the Engineers' Club, Manchester.* "The Value of Organized Research in the Rubber Industry." B. D. Porritt.

Feb. 5 *To be read at the Engineers' Club, Manchester.* Conjoint meeting with the Society of Chemical Industry.

March 7 *To be read at the Engineers' Club, Manchester.* Short Papers' Night.

April 4 *To be read at the Engineers' Club, Manchester.* "Gutta Percha—Its Characteristics and Manufacture." A. E. Penfold.

Scottish Section

1931

Oct. 14 *To be read at the Caledonian Hotel, Edinburgh.* Not arranged.

Nov. 18 *To be read at the Institution of Engineers and Shipbuilders, Glasgow.* Not arranged.

Dec. 16 *To be read at the Caledonian Hotel, Edinburgh.* Not arranged.

1932

Jan. 21 *To be read at the Institution of Engineers and Shipbuilders, Glasgow.* "The Treatment of Cloth Previous to Rubber Proofing." J. Y. Stewart.

Feb. 25 *To be read at the Caledonian Hotel, Edinburgh.* "Problems in the Manufacture of Rubber Goods as Dealt with in the Laboratory." G. W. James.

March 25 *To be read at the Institution of Engineers and Shipbuilders, Glasgow.* Not arranged.

New Books and Other Publications

A Guide to the Literature on Rubber. Letter Circular 305. Department of Commerce, Bureau of Standards, Washington, D. C.

This is a 13-page mimeographed memorandum prepared to assist readers unfamiliar with rubber technology in obtaining recent and authentic information relating to the production, manufacture, and properties of rubber and rubber products. The list includes only recent books, current periodicals, and other publications which are liable to be readily accessible and useful to American readers. Only casual reference is made to patent literature. [From *India Rubber World.*]

Annual Survey of American Chemistry. Volume V, 1930. Edited by Clarence J. West, Foreword by Harry A. Curtis, Chairman, Division of Chemistry and Chemical Technology. Published for National Research Council by The Chemical Catalog Co., Inc., 419 Fourth Avenue, New York, N. Y., 1931. Cloth, 629 pages, 5 by 8¼ inches. Author and subject indices. Price, $5 net.

In this annual publication the results of research in 40 branches of chemical technology are systematically outlined by 46 outstanding specialists. The enlargement of the amount of research recorded in successive issues of this annual is said in the foreword to indicate probably both an increase in the volume of research in America and more diligence on the part of the contributors in covering their topics.

A full review of rubber research is given by John T. Blake, research chemist, Simplex Wire & Cable Co., Boston, Mass. The topics in the review of rubber are as follows: Cultivation, structure, physics, synthetic rubber, vulcanization, accelerators, aging and antioxidants, compounding ingredients, electrical insulation, physical testing, chemical analysis, reclaimed rubber, etc. [From *India Rubber World.*]

Modern Progress in Rubber Compounding. By Charles R. Boggs. Published by the Simplex Wire & Cable Company, 201 Devonshire Street, Boston, Mass., 1931. 28 pp. For free distribution.

After some brief comments on rubber itself, its physical structure and behavior, and the mechanism of vulcanization, the author discusses the salient developments in rubber compounding, with particular reference to insulation. Some of the advances brought about by the use of accelerators, antioxidants, new vulcanizing materials, new compounding materials, etc., are discussed and experimental data which demonstrates the improved physical, electrical, and aging characteristics are given. Accelerated aging tests are treated in some detail, with an appendix presenting various opinions as to their value. This is a reprint of a paper given by the author before the Signal Section of the American Railway Association on May 13. [From *The Rubber Age* of New York.]

Elektrophorese, Elektro-Osmose, Elektrodialyse in Flussigkeiten. (Electrophoresis, Electro-osmosis, Electrodialysis in Fluids.) By Drs. P. H. Prausnitz and J. Reitstötter. Published by Theodor Steinkopff, Dresden and Leipzig, Germany, 1931. Paper, 324 pages, 6 by 8¾ inches. Illustrated.

In this present volume of the Scientific Research Reports, of the Natural Science Series, the authors have endeavored to present both the scientific discoveries and observations as well as the technical inventions in the field of the electro-chemistry of colloids and to relate the trends of research work and methods in order to give an objective picture of the state of development of this branch of investigation.

In their selection of works and articles of which they have made use in this book, the authors have, on the whole, confined themselves to the most important of those that have appeared during the present century, up to November, 1930, while special attention has been paid to those works and articles of the last decade.

The work has been divided into five parts: I General, II Electrophoresis, III Electro-osmosis, IV Electrodialysis, and V Technical applications with special reference to patent literature. Mention is made, of course, of work in connection with Hevea latex and rubber, and in Part V we find listed a series of American and foreign patents with brief explanations, relating to electrical dispersions and depositions of rubber.

The value of the book is enhanced by a fairly extensive bibliography and separate indices of patents, authors, and subjects. [From *India Rubber World.*]

Tentative Specifications for Cotton Rubber-Lined Fire Hose for Public and Private Fire Department Use. A. S. T. M. Designation: D 296–31 T. Published by American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa.

This is the 1931 revision and covers $1^1/_2$, 2, $2^1/_2$, 3, and $3^1/_2$ inch single, double, or triple-jacketed cotton rubber-lined fire hose suitable for use in public or private fire departments. [From *India Rubber World.*]

Sixth Report on Native Rubber Cultivation. Published by the Division of Agricultural Economics of the Department of Agriculture, Industry, and Commerce, Buitenzorg, Java. 1931. 12 pp.

The falling off in native rubber production in the Dutch East Indies last year is shown in detail in this report, which covers the period from September, 1930, to March 18, 1931. A brief supplement to the report, written as of April 4, 1931, points out that the new price fall of rubber will probably result in a new decrease in the export of native rubber, particularly because every price fall is in percentage far heavier for the native rubber than for the standard product. "The question arises," the report concludes, "whether at this low price level the estates will also contribute to a recovering of the market by a considerable reduction of their total production." [From *The Rubber Age* of New York.]

Studies in the Artificial Control of Raw Material Supplies: No. 2, Rubber. By J. W. F. Rowe. Published by the London & Cambridge Economic Service, Houghton Street, Aldwych, London, W. C. 2, England. 1931. 88 pp. 5s.

A study of the rubber industry during the past ten years, this publication gives a detailed account of the Stevenson scheme, its history, working, and effects on the industry. Relevant statistics are included, and a lengthy chapter on the Dutch native rubber industry is extremely interesting. It is Mr. Rowe's opinion that the small native rubber holdings in Malaya will in the future become rapidly less productive and decline in importance as compared to the large estates. [From *The Rubber Age* of New York.]

Organisation des Weltkautschukmarktes. By Franz Juda. Publishers, Buchdruckerei Bavaria G. m. b. H., Wurzburg. Paper, $8^1/_4$ by $5^5/_8$ inches, 104 pages, tables, bibliography.

The rubber situation and particularly the rubber market and its organization, is carefully gone into. Starting with an introductory chapter on sources and production of output of crude rubber, the author then discusses the factors governing supply and demand; prices and monopoly tendencies among producers and manufacturers; the organization of the market, that is, dealers,

brokers, stocks, qualities, contracts, exchange, etc.; and finally the development of the different markets in the East and in the consuming countries.

Opinion of the leading markets is as follows: The position of London is assured as long as it has the planting companies in its hand and the estates can hold their own against native output. The growing importance of Europe as consumer of crude rubber as compared with America is another factor in London's favor. The factors tending to weaken London are precisely those that spell strength for Singapore; while, finally, New York depends on the position of America as consumer.

The author complains of the lack of reliable data so necessary in organizing the market and points to the need of such organization in different countries, and more particularly for native rubber.

A number of tables relating to areas, outputs, stocks, consumption, prices, reclaim, etc., are appended, which together with the bibliography, add value to the booklet. [From *India Rubber World.*]

Seventeenth Annual Report. Published by the International Association for Rubber and Other Cultivations in the Netherlands Indies, N. Doelenstraat 5, Amsterdam, Holland. 1931. 56 pp. For distribution to members.

Problems of labor, taxation, etc., on rubber estates are reviewed in this report in addition to its presentation of important statistics on production in the Netherlands East Indies. At the end of 1930, this association had 203 company members and 60 individual members. Suggestions offered for the improvement of Dutch East Indies statistics are treated more fully on page 227 of this issue. A 12-page report of the association's propaganda department is appended and gives a summary of work done to increase the use of rubber in various directions. [From *The Rubber Age* of New York.]

Handbuch der Kautschuk-Industrie und Asbest-Industrie. (Handbook of the Rubber and Asbestos Industries), edited by Walter Lindemann and published by the Atlas-Verlag Dr. Alterthum & Co., Berlin W 15, 1931; 320 pages, including advertisements. Price, 15 gold marks ($3.50).

This is an excellent and very complete commercial handbook. It contains a foreword by Willy Tischbein, short introductory articles on rubber and asbestos by the editor, and the following carefully arranged lists, indexes, and tables: Firms dealing in rubber and asbestos goods, their addresses, names of their chief officers, branches, and products; survey of the bases of the mercantile policies of Germany regarding German export trade to all important foreign countries; German tariff rates on products of the rubber and asbestos industries; German tariff classification of products of the rubber and asbestos industries, according to types of goods; names of firms; sources of supply of raw and manufactured materials and mechanical equipment; industrial and scientific organizations, trade unions, periodicals, etc.; and trade names and trade marks.—HARRY L. FISHER.

1931 Year Book. Published by the Tire & Rim Association, Inc., 1401 Guarantee Title Building, Cleveland, O. 1931. 154 pp. $2.

This annual volume contains the usual data on standard rim contours, gauges and tolerances, loads and inflations, valves, etc., on passenger car, truck, bus, airplane, and motorcycle tires. A 40-page appendix includes information about European rim contours, loads and inflations, embodying the latest data available. [From *The Rubber Age* of New York.]

Tire Table of Balloon Tires. National Rubber Machinery Co., Akron, O.; Clifton, N. J.; and Columbiana, O.

This pocket folder gives the sizes of balloon tires on domestic and foreign cars, and the makers of the cars that have used them for the five years from 1927 to 1931 inclusive. [From *India Rubber World.*]

Cycles in the Automobile Pneumatic Tire Renewal Market in the United States. By Royal E. Davis. 1931. 10 pp.

As statistician of the Goodyear Tire & Rubber Company, Mr. Davis has made extensive researches into the available figures on tire marketing in this country. This paper presents the statistical technic and the interpretation of an index he has constructed of renewal pneumatic tire sales activity between 1921 and 1930. He concludes that tire activity has moved two to six months ahead of general business in the past, both on the down swing and the up swing. "Viewing 1931," he comments, "on the whole I expect renewal tire sales activity to improve steadily throughout the year. While this improvement is not likely to be so swift as the recovery following depression periods in the past, it seems reasonable that 1931 should be a more active year than 1930, but less active than 1929." The paper is reprinted from the March supplement of the *American Statistical Journal.* [From *The Rubber Age* of New York.]

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the July 10 and 20, August 10 and 20, and September 10 and 20, 1931, issues of *Chemical Abstracts* and with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

The lipin of Hevea latex. E. RHODES AND R. O. BISHOP. Rubber Res. Inst. Malaya, *Quart. J.* **2**, 125–35(1930).—In expts. on serum products obtained by the EtOH-coagulation of latex, Belgrave and Bishop obtained a waxy product, the quantity of which was too small for detailed examn. (cf. *C. A.* **18**, 3738). The present paper describes the prepn. of a relatively large quantity and its proximate analysis. Latex poured slowly into EtOH (2.5 vols.), the rubber pressed, the alc. serum filtered through coarse paper, concd. *in vacuo* at 40° (higher temps. cause darkening) to $^1/_{12}$ its vol., cooled, extd. 3 times with Et_2O, the combined exts. evapd. rapidly to dryness at room temp., dried *in vacuo*, yields a golden-yellow, transparent *wax* (I). This process was repeated until enough wax was collected. The accumulated yield was approx. 0.2% of the latex. This cold extn. does not remove all so-called resins (cf. Dekker, *C. A.* **20**, 310), but only substances readily dispersible in water, which are more like lipins than fats or fatty acids. I has an earthy taste, and is readily dispersed in water. Its Et_2O soln. emulsified with water, after the Et_2O is removed, leaves a permanent yellowish suspension which resembles a soap soln. in that it foams and bubbles. I cannot be extd. from this suspension by Et_2O. I let stand with a little water forms a jelly. A 0.2% suspension in water (the concn. in latex) has only 0.5 the surface tension of water, and with greater concns. the surface tension is correspondingly lower. Concd. mineral acids and HCHO, but not AcOH, flocculate completely its aq. suspensions. Thus a 2% suspension had a p_H value of 5.8, and on addn. of acid the color became whiter, at p_H 2.5 curds became visible and at p_H 1.9–2.0 there were large curds and a clear liquid. These curds can be extd. with Et_2O. $CaCl_2$ and $MgCl_2$ also cause complete flocculation to an Et_2O-sol. product. I softens at 60°, but has no well-defined m. p., and melts and chars simultaneously at a high temp., with odor of hot lard, with ultimate formation of a coke. With concd. HNO_3, I turns bright cherry-red and disintegrates, a dark red oil seps. and if the reaction mixt. is heated, NO is evolved, the oil disappears and on cooling a bright yellow *wax* sol. in Et_2O and warm EtOH is formed. Like cerebrosides, it gives with concd. H_2SO_4 a deep purple-red, and the color appears soonest in the presence of sucrose. It gives a strong Molisch reaction, and a negative protein test. Its original I no. was 97, and if its aq. suspension is flocculated by acid and extd. with Et_2O, 95% of the substance is recovered, with an I no. of 102. The N, P and ash contents of I were 0.54–0.59, 1.59–1.72 and 4.60–5.35%, resp., which suggest the presence of lipins, but not in a pure state. Extn. of I with acetone and of the residue with Et_2O gave a 41.7% yield of acetone-insol., Et_2O-sol. components contg. 0.88% N and 2.56% P; this does not correspond to a pure phosphatide. The original acid, ester and sapon. nos. of I were 14, 159 and 173, resp., the Et_2O-sol. unsaponifiables 1.1%, and Et_2O-sol. acids 71%, and these values indicate the presence of a substance not normally present in fats, waxes and pure animal phosphatides. Sepn. by the Pb-salt-ether method of the mixed acids obtained by alk. hydrolysis yielded 95% liquid and 5% solid acids, with I nos. of 123 and 59, resp. The solid acids were white and hard. Bromination of the liquid acids gave 2.5% of possible hexa- and octabromides. Judged by the soly. of the Et_2O-sol. bromides in petr. ether, a large proportion of acids of the linoleic series was present. The mixed acids subjected to alcoholysis by the Twitchell method, the acids sol. in abs. EtOH satd. with HCl gas, cooled, dild. with water, extd. with Et_2O, the ext. washed free of acid, dild. with EtOH and titrated, showed 97% esterifiable; hence resin acids were present in

negligible proportion, and the mixed acids were true fatty acids. I was dissolved in abs. EtOH, satd. with dry HCl, refluxed 5 hrs., the EtOH eliminated, water added, the esters (a floating oil) were removed by Et_2O and the humus substances by filtering. With proteins absent, the humus substances showed the existence of hexose in I. The filtrate reduced Fehling soln. and yielded a cryst. *osazone* (II) resembling those of galactose and maltose. A reaction characteristic of levulinic acid was also obtained. The Florence test was pos., and alc. $HgCl_2$, H_2PtCl_6, picric acid and phosphotungstic acid gave ppts., the last ppt. contg. 71% of the total N, all of which results indicate the presence of an unidentified base. The filtrate with Br water and H_2SO_4 gave pos. color reactions with alc. *o*-$HOC_6H_4CO_2H$ and KBr, resorcinol, thymol and β-naphthol and together with a pos. acrolein test of I indicated the presence of glycerol. This was not, however, proved conclusively. Hydrolysis of I by alc. KOH pptd. a sticky *substance* (III), and when the EtOH was eliminated and water added to ext. unsaponifiables, the sticky substance dissolved. After removal of the unsaponifiables, the aq. liquor and fatty acids were neutralized, and then failed to reduce Fehling soln. III contains 98% of the P originally present in I. Aq. III did not reduce Fehling soln., but when heated with 10% HCl and neutralized it did reduce, and formed II. Estd. by reduction of Fehling soln., the hexose was 8% (based on the fat). The sapon. liquor after removal of EtOH, addn. of water, pptn. and removal of fatty acids (odor of sugar) and inversion with HCl reduced Fehling soln., and contained 1.6% hexose, *i. e.*, the total hexose was 9.6%. This is a low value, but the sugar is not present originally as a reducing agent. Ten % HCl added to an aq. suspension of I, heated to boiling until the curd rose to the surface, and the curd removed with Et_2O, gave a liquid contg. 3.6% hexose (based on I). If heating is continued after the curd changes in consistency and rises, it changes to an oil, and the reducing power of the liquid becomes much greater. I in Et_2O poured into water, the Et_2O evapd. at 70°, flocculated with excess dil. HCl, extd. with Et_2O, the ext. poured into water, the Et_2O evapd., and the dispersion and extn. carried out 5 times, yielded a product which could no longer be dispersed and which had lost most of its reducing sugar, nearly all its ash and some of its P and N. The expts. in general show that I is not a pure phosphatide, but is a peculiar complex mixt. of fatty acids, sugar, Et_2O-sol. P and N, with properties abnormal to fatty substances except lipins. A comparison of the properties of I with those of other plant lipins (*Z. physiol. Chem.* **20,** 478(1895); **40,** 101(1903); Whitby, *C. A.* **19,** 3386; Maclean, Lecithin and Allied Substances, *C. A.* **21,** 2002; Sakaki, *C. A.* **7,** 2231) shows a striking parallelism. By expressing the analytical results in the following way (all in %): P as glycerophosphoric acid 9.55, N as choline 5.06, unsaponifiable 1.10, fatty acids 71.00, sugar 10.00, ash as K_2O 3.55, the sum is 100.26. This accounts for all components, and it allows for the presence of free fatty acids, some fatty acid soap and fatty acids united with sugars, all of which seem necessary to explain the properties of I. The expts. are being continued to identify the individual components. C. C. DAVIS

Observations on the effect on vulcanization of the lipin of Hevea latex. B. J. EATON, E. RHODES AND R. O. BISHOP. Rubber Res. Inst. Malaya, *Quart. J.* **2,** 136–8(1931)(Six pages of charts).—It has already been shown (cf. B., *C. A.* **18,** 3739) that rubber prepd. from latex coagulated with EtOH vulcanizes more rapidly than crepe prepd. by ordinary acid coagulation. The present work shows that rubber prepd. with EtOH has an optimum cure at 60 min. compared with 90 min. at 148° for standard plantation crepe in a mixt. of rubber 100, S 10, *i. e.*, a slower rate than "slab" rubber and approx. the same as fine hard Para. The rate of vulcanization of EtOH-coagulated rubber prepd. from different days' latex was practically const., and differences in details of prepn., such as time of soaking in EtOH, the diln. of the EtOH and time of drying, had no significant effect. The tensile strength and other phys. properties of the vulcanizates were normal. Addn. of *Hevea* lipin (cf. preceding abstr.) to EtOH-coagulated rubber accelerated its rate of vulcanization. One % had a relatively greater effect than 2%, and 2% a relatively greater effect than 3% and the acceleration was of the same order of magnitude as that from the addn. of lipin to slab rubber. The effect of lipin in ordinary plantation rubber-S mixts. depends upon the rate of vulcanization of the rubber, *e. g.*, pale crepe with an optimum cure of 100 min. is not accelerated by 1% lipin, while 2% accelerates the cure to 90 min. On the other hand, 1% lipin accelerates "slab" crepe from an optimum cure of 40 min. to 30 min. Mixts. of rubber 100, S 10, ZnO 5 are accelerated to a greater extent by 1% lipin than corresponding rubber-S mixts. with and without ZnO, and in normal plantation crepe the acceleration is increased so much that the optimum cure is almost as short as that of a corresponding mixt. of slab rubber, *e. g.*, the 20-min. cure was more advanced than the 70-min. cure. *Hevea* lipin is probably related to egg lecithin, and it was found that com. lecithin accelerated the rate of vulcanization of ordinary crepe more than did lipin. The effect of adding lecithin to crepe,

smoked sheet and slab crepe while mixing on hot rolls is almost like that of the lipin, for in each case the plastic mass becomes opaque and crumbles. On further mastication, with the temp. not over 55°, the crumbs again assume the plastic form of hot masticated rubber. If, however, the rubber is first mixed with S or with S and ZnO, the crumbling is much less, and the mass, though "greasy," adheres tightly to the rolls. The similarity in behavior of lecithin and *Hevea* lipin suggests closely related chem. properties. The results are shown graphically in detail. C. C. DAVIS

A preliminary study of the bacteriology of Hevea latex. A. S. CORBET. Rubber Research Inst. Malaya, *Quart. J.* **2**, 139–55(1930).—The present paper describes further diagnostic characteristics and behavior under various conditions of numerous microorganisms isolated from samples of *Hevea* latex from different parts of Malaya (cf. *C. A.* **24**, 1761). The results are of importance in relation to natural coagulation, preservation, anticoagulants and the inhibition of bubble formation in sheets. The microörganisms isolated included *Gaffkya verneti*, *Micrococcus eatoni* (I), *Micrococcus ridleyi*, *Micrococcus epimetheus* (II), *Micrococcus chersonesia*, *Alcaligenes denieri*, *Bacillus pandora* (III) and *Torula heveae*. All were Gram-pos., few liquefied gelatin and only II and III reduced nitrates, formed indole and fermented sugars. I gave the most pronounced yellow color in latex, but the pigment is sol. in water and disappears in the com. prepn. of rubber. II has properties similar to III (already described, *loc. cit.*), *i. e.*, it brings about acidification and flocculation of latex. II also forms gas in latex, and this may explain the formation of bubbles in sheet rubber. II grows well with p_H at 4.7–9.0, but at 4.4 it disappears. Gas formation from II is completely inhibited, therefore, by maintaining the p_H value of the coagulating tank not over 4.4. No exptl. evidence was obtained to uphold the common assumption that bacterial acidification of latex resulted from decompn. of methyl-*l*-inositol (IV), for no acid was formed by inoculation of a liquid contg. IV with III, though much acid was formed when latex serum from frozen latex was innoculated with III. Acid but no gas was formed when II was added to aq. IV contg. $MgHPO_4$ and KCl, but there was no action in the absence of the $MgHPO_4$. Of the latex substances likely to yield acid, IV alone is present in sufficient quantity, and its resistance to attack by II is great. It is possible therefore that there is some other factor which plays a part in the decompn., a view which is supported by the behavior of II.
C. C. DAVIS

Observations on the coagulation of Hevea latex. R. G. FULLERTON. Rubber Research Inst. Malaya, *Quart. J.* **2**, 156–81(1931). (Four extra pages of diagrams.)—The continuity of the course of coagulation of (1) fresh latex, (2) preserved latex and (3) centrifuged latex by the addn. of acids was studied, and the p_H values of the various zones in the irregular series were detd. by means of the quinhydrone electrode. The technic and the app. were nearly the same as those used by Biilmann and Tovborg-Jensen for soil-water mixts. (cf. *Trans. 2nd Commission Intern Soc. Soil Science* **1927**). With fresh latex dild. to a rubber content below 10%, the transition from the 1st liquid zone to the 1st coagulation zone is accompanied by a progressive series of changes in the state of dispersion, and is also irregular, for the p_H values of the transitional stages vary in latex collected on different days. In most cases when the series is examd. in the direction of diminishing p_H, there is a gradual progression from complete dispersion to complete coagulation through regions of partial flocculation, complete flocculation and incomplete coagulation. Generally the range covered by this transitional stage is from p_H 5.30, at which point a sepn. of the rubber component from the dispersion is first visible at p_H 4.87, which marks the beginning of complete coagulation. These values agree well with those of van Harpen (cf. *Arch. Rubbercultuur* **13**, No. 1(1929)). The dry rubber content of fresh field latex has a marked influence on the course of the irregular series. With latexes whose rubber content varies from 4 to 35%, the range of p_H values which define the transitional stage between the 1st liquid and the 1st coagulation zones increases with increase in the rubber content. On the other hand, with increasing rubber content the range of p_H values which define a condition of flocculation decreases until, with latexes contg. over 15% rubber, this stage disappears completely. With latexes contg. 20–35% rubber, there is no 2nd zone of complete dispersion. Unlike latexes of greater diln., in which the dispersion is complete in the range of the 2nd liquid zone (p_H approx. 3.5–1.0) and which remain stable for several days if the p_H value is kept const., with latexes contg. more than 20% rubber coagulation takes place for the same approx. range of values, and the extent of the coagulation depends upon the rubber content. The appearance of a flocculation stage of fresh field latex is assocd. only with the transition from the 1st liquid zone to the 1st coagulation zone, regardless of the degree of diln. of the latex. Expts. on the irregular series of boiled latex ("B" liquid) confirmed the observations of other investigators that such latex does not coagulate until a p_H value of 0.80 is reached, and that the addn. of soaps such as Na oleate restores

normal coagulation in the 1st zone. This was compared with the effect of adding Na oleate to fresh field latex which had been dild. to the same rubber content as the "B" liquid. Measurements were also made of the changes in p_H which occur in fresh latex heated to various temps. and allowed to cool to the original temp. With regard to the course of the irregular series, it was found that latex preserved with NH_3 behaves in much the same way as fresh field latex. On the other hand, if latex preserved with HCHO is dild. to a rubber content below 10%, coagulation by acid does not occur at any p_H value below 7.0. To approx. the same ranges of p_H values within which fresh latex of the same diln. shows 2 well-defined coagulation zones, there correspond 2 zones of complete coagulation with latex preserved with HCHO. Even when the latex is not dild., coagulation by acid takes place only after mech. kneading of the flocculated mass. Fresh latex treated with NaOH behaves in the same way. On the other hand, storage for 1 month or more of latex preserved with NaOH restores normal coagulation within these 2 zones, though the course of the series is almost continuous, with no 2nd liquid zone. In such latex, clot formation by the addn. of acids can begin at a p_H value on the alk. side of neutrality. Latex sepd. into cream and skim by centrifuging was also studied. Cream latex behaves like latex preserved with NaOH which has been stored for a month or more, insofar as there is practically no break in the continuity of the series. On the other hand, with the skim fraction the irregularity of the series is just as well marked as with fresh field latex. These results apply to latexes dild. to 4% rubber. The results are tabulated in complete detail. C. C. DAVIS

The treatment of latex concentrates. JOACHIM FISCHER. *Kunstoffe* **20**, 1–2 (1930).—A short discussion of present developments in processing Revertex and Revultex. C. C. DAVIS

Micromanipulations of latex in the dark field. E. A. HAUSER. *Rubber Chemistry & Technology* **4**, 219–22(1931).—See *C. A.* **25**, 1409. C. C. DAVIS

The constitution of rubber. R. PUMMERER. *Rubber Chemistry & Technology* **4**, 206–10(1931).—See *C. A.* **25**, 1410. C. C. DAVIS

The fusion curve of natural rubber. G. V. SUSICH. *Rubber Chemistry & Technology* **4**, 211–2(1931).—See *C. A.* **25**, 1410. C. C. DAVIS

The evaluation of raw rubber. G. MARTIN. *Trans. Inst. Rubber Ind.* **6**, 298–316 (1930).—A crit. review and discussion. A large variety of tests has been suggested for the evaluation of raw rubber for general purposes, but only those which show: (1) how the rubber is likely to behave in mfg. operations; (2) any abnormality in quality; (3) the aging properties of the rubber; and (4) the behavior of the rubber with accelerators, are necessary in formulating a scheme for evaluating the quality of rubber from a practical point of view. These 4 important properties of a rubber may be judged by: (1) a mastication test; (2) a vulcanization test in a rubber-S mixt.; (3) an artificial aging test in a rubber-S mixt.; and (4) a vulcanization test in an accelerated mixt. The most suitable conditions for carrying out each of these tests are discussed at length, and the results which may be obtained are illustrated by tests on air-dried and smoked sheet. Particular attention is paid to plasticity. By applying the equation of Taylor for the motion of the top disk in the compression of a plastic (cf. Bakerian Lecture to the Royal Soc. **108**, 12) to plasticity measurements by the van Rossem method (van Rossem and Meijden, cf. *C. A.* **22**, 3063; **23**, 2068), it is shown that the time required to compress different samples of rubber from 1 definite thickness to another is directly proportional to the apparent viscosities under the particular load and at the temp. chosen, and this was confirmed with many tests. For the same reason the time with the Williams app. (cf. *C. A.* **18**, 1763) to compress different samples from 1 thickness to another is directly proportional to the apparent viscosities. There are accordingly 3 methods available for measuring the apparent viscosity of rubber in units which are directly proportional to one another and to abs. units. Compression methods are preferable to extrusion methods, because they are more convenient and probably more accurate. Of the 2 compression methods, the Williams test is preferable to the van Rossem modification because the results are proportional to the av. viscosity over a wide range of loads, and not to a single viscosity at an arbitrary load. The results must be expressed in terms of the time interval between 2 fixed thicknesses, and not, as is more usual, in terms of the final thickness after a fixed time interval. A plasticity detn. is of value only if it bears a relation to the behavior of rubber in mastication, in which connection expts. (work of Ceylon Rubber Research Scheme) so far show that a hard rubber usually requires longer mastication than a soft one, though the work is not far enough advanced to give a method for predicting from the hardness the mastication which will be required. A mastication test under the most accurately standardized conditions is therefore still necessary for evaluating raw rubber. With the conditions of mastication defined, the rubber may be masticated (1) for a definite time and the result expressed as plasticity,

or (2) until it reaches a definite plasticity and the result expressed as the mastication required. Method (2) is preferable, because the results are in practical units. In lab. tests, it is necessary only to det. the plasticity at 2 stages approaching the plasticity required, from which the mastication required can be calcd. on the assumption of a straight-line function. This relation is not obvious from the usual mestication plasticity curves, because the results are in time units (corresponding to viscosity) instead of in the reciprocal vol. units (corresponding to fluidity). When the data of Griffiths (cf. *C. A.* **20**, 2094) and of Fry and Porritt (cf. *C. A.* **22**, 4870) are converted to their reciprocal values, straight-line relations are obtained, and for this reason it is preferable to express plasticities as rates of flow instead of times of flow, for both the compression and the extrusion method. A further advantage is that high values represent high plasticities and *vice versa*. By this method, tests show that air-dried sheet requires about 15% more mastication than smoked sheet to reach a definite plasticity. Nothing is known of the principles of elastic deformation, and its measurement is not of use in evaluating raw rubber. It is usually assocd. with plastic deformation, and the more rapid the deformation the greater is the elastic deformation. Methods of measuring plasticity by the final thickness (Williams test) show the total flow from both plastic and elastic deformation, whereas measurement of the rate of flow may involve only plastic flow, since the rubber probably remains in the same state of elastic tension throughout.

C. C. Davis

The surface tension of rubber solutions. C. W. Shacklock. *Trans. Inst. Rubber Ind.* **6**, 259–70(1930).—A soln. of disaggregated rubber should have the same surface tension as one of the same rubber not disaggregated, whereas the surface tension of a soln. of depolymerized rubber should be different from that of a soln. of the same rubber before depolymerization. It should therefore be possible to detect depolymerization, *e. g.*, to decide whether mastication causes depolymerization, by the viscosities of similar solns. of a rubber before and after the supposed depolymerization. Preliminary expts. showed that both the drop method and the capillary rise method are unreliable with rubber solns., and the bubble pressure method was used in the final expts. The app. of Sugden (cf. *The Parachor and Valency*) is satisfactory if (1) O, CO_2 and H_2O are removed from the air; (2) the inert gas is then satd. with C_6H_6; and (3) $PhNO_2$ is used as the manometric liquid. The *app.* and the *technic* thus modified are described in detail and illustrated. In all cases 3% solns. in C_6H_6 at 20.8° of pale crepe in the following conditions were measured: (1) unmasticated crepe; (2) crepe extd. with acetone, dried *in vacuo*, dissolved in C_6H_6, pptd. with EtOH (approx. $^2/_3$ pptd.), dried and the process repeated twice; (3) crepe masticated cold for 2 hrs.; (4) crepe masticated at 99° for 2 hrs.; (5) soln. (1) exposed to ultra-violet light until it was almost as mobile as C_6H_6; (6) crepe heated 10 hrs. in air at 155–60°; and (7) crepe heated 10 hrs. *in vacuo* at 155–60°. The following values are the ergs per sq. cm. for pure C_6H_6 and the 7 solns. above: 28.80, 28.86, 28.86, 30.74, 29.34, 28.51, 28.91, 28.98. The surface tension of rubber is not affected by resins, by fractional pptn. nor by absorption of O (cf. Fry and Porritt, *Trans. Inst. Rubber Industry* **3**, 203(1927)), whereas mastication does change the surface tension. A lowering of the viscosity of a rubber soln. may have several causes, and is commonly attributed to disaggregation, which is supported by the results with (5) and (6) (*loc. cit.*). If depolymerization occurred in both solns., there would have been a change in surface tension. The slight lowering of the surface tension by ultra-violet light may be a result of depolymerization. Since absorption of O does not change the surface tension, neither disaggregation nor O absorption alone affects surface tension, whereas a combination of these effects, *e. g.*, by ordinary mastication, does change the surface tension. Mastication is not therefore brought about by mech. action or by absorption of O alone, but only by the simultaneous action of these 2 factors. This is supported by the expts. of Daynes (cf. *C. A.* **22**, 3802). Mastication is more extensive when the rubber is cold, and the fact that the lower the temp. the greater the absorption of O may explain the difference in the surface tensions of cold and hot masticated rubber solns. Though O absorption does not affect surface tension, the more rapid soln. and lower viscosity indicates that it does cause disaggregation. The increase in surface tension brought about by hot and cold mastication is not explained, though possibly a compd. between disaggregated rubber and O is formed from O_3 produced by elec. effects. Mastication is therefore necessary, for otherwise the O stays in soln. in the rubber. When rubber is washed in rolls, no elec. effect is possible, and therefore the rubber is not masticated during the washing. The fact that the surface tension of some of the solns. is the same as that of C_6H_6 supports the idea of Stamberger and Blow (cf. *C. A.* **23**, 4846) that the "structure" of rubber persists in dil. solns. A general discussion follows the paper.

C. C. Davis

The compressibility of rubber. L. H. ADAMS AND R. E. GIBSON. *Rubber Chemistry & Technology* **3**, 555–62(1930).—See *C. A.* **24**, 4185. C. C. DAVIS

Phenomena of the mechanical deformation of rubber. H. MARK AND E. VALKO. *Rubber Chemistry & Technology* **4**, 54–63(1931).—See *C. A.* **25**, 434. C. C. DAVIS

The constitution of rubber according to its swelling in liquids. PAUL BARY. *Rubber Chemistry & Technology* **3**, 576–85(1930).—See *C. A.* **24**, 4954. C. C. DAVIS

Influence of the amount of the surplus liquid on the swelling maximum of rubber jellies. C. M. BLOW AND P. STAMBERGER. *Rubber Chemistry & Technology* **4**, 64–74 (1931).—See *C. A.* **23**, 4846. C. C. DAVIS

An investigation of the viscosity of rubber solutions. C. M. BLOW. *Rubber Chemistry & Technology* **3**, 604–11(1930).—See *C. A.* **24**, 4661. C. C. DAVIS

The viscosity of rubber solutions under the influence of benzoyl peroxide. G. FROMANDI. *Rubber Chemistry & Technology* **4**, 8–12(1931).—See *C. A.* **24**, 4956. C. C. DAVIS

The protective action of some antioxidants. II. The metal halide compounds of some protective agents against aging, with special reference to adolnaphthylamine. F. KIRCHHOF. *Rubber Chemistry & Technology* **4**, 239–47(1931).—See *C. A.* **25**, 2593. C. C. DAVIS

The action of solvents with rubber. P. STAMBERGER AND C. M. BLOW. *Rubber Chemistry & Technology* **4**, 223–8(1931).—See *C. A.* **25**, 1410. C. C. DAVIS

The oxidation of rubber at atmospheric temperatures. W. C. DAVEY. *Rubber Chemistry & Technology* **4**, 229–38(1931).—See *C. A.* **25**, 840. C. C. DAVIS

Studies in the oxidation of rubber mixings. W. CECIL DAVEY. *Rubber Chemistry & Technology* **3**, 563–75(1930).—See *C. A.* **24**, 4660. C. C. DAVIS

Alternating behavior of fatty acids in rubber compounds. T. L. GARNER. *Rubber Chemistry & Technology* **3**, 612–4(1931).—See *C. A.* **24**, 4662. C. C. DAVIS

The dispersion of gas black and the physical properties of rubber mixtures. E. A. GRENQUIST. *Rubber Chemistry & Technology* **4**, 29–38(1931).—See *C. A.* **24**, 4958. C. C. DAVIS

Development in the carbon black industry. GEORGE REID. *Refiner and Natural Gasoline Mfr.* **10**, No. 3, 148(1930).—The mechanism of prepn. and the properties of C black for the rubber trade are given. J. L. ESSEX

Effect of temperature, pressure and frequency on the electrical properties of rubber. H. L. CURTIS, A. T. MCPHERSON AND A. H. SCOTT. *Phys. Rev.* [2], **33**, 1080(1929).—The dielec. const., power factor and resistivity of rubber depend on the percentage of S used in its vulcanization, on the temp. and pressure, and, for the 1st 2 properties, on the frequency at which measurements are made. B. C. A.

Reënforcement. A critical survey. F. H. COTTON. *Trans. Inst. Rubber Industry* **6**, 248–58(1930).—The most important evidence to be found in the literature indicates that the valuable properties imparted by reënforcing fillers are attributable to the increase in surface energy of the mixt. The chief cause of the increase in tensile strength of a reënforced mixt. is the shortening of the ultimate elongation by the filler, as suggested by Blake (cf. *C. A.* **22**, 4876), which results in the distribution of the stress over a greater cross-sectional area. The addnl. work required to rupture is expended in overcoming 4 factors: (1) the forces of adhesion between the rubber and that portion of the filler which is wetted (those forces may exceed the force of cohesion between the rubber particles), (2) the interfacial tension between the filler and rubber or air (with incompletely dispersed fillers), which resists any tendency toward an increase in the total surface area exposed by the rubber and filler (work must be expended in forming vacuoles on stretching), (3) the friction between flocculated filler particles incompletely wetted by rubber, (4) the friction between rubber particles which are undergoing reversible plastic flow around the filler particles. If the rubber adheres powerfully to the surface of the filler, there must be a type of flow analogous to the flow of a viscous liquid in a small tube, when the rubber stretches around the filler particles. The higher the loading, the thinner are the individual films of rubber which surround the filler particles, and the greater is the energy required to promote flow in the rubber. The addnl. work to overcome friction between the flocculated particles is probably dissipated completely as heat, and the displacement of flocculated particles is largely permanent, with the result that there is a permanent set. The viscous elastic flow of the rubber around the particles is largely reversible, but the higher the loading with a reënforcing filler the greater should be the viscous forces opposing motion. This addnl. energy is dissipated as heat and contributes to the hysteresis loss (cf. Dawson, *C. A.* **20**, 3838; Parkinson, *C. A.* **24**, 2636). Expts. in progress indicate that no reënforcing filler is capable of increasing the capacity of vulcanized rubber to accumulate energy, and preliminary results suggest that there is a relation between the reënforcing properties of a powder as measured by the proof

resilience (cf. Wiegand, *C. A.* **19**, 3386) and the hysteresis loss. The advantage in reënforcing rubber with a filler lies not only in the greater resistance to wear, *i. e.*, the greater energy absorption capacity, but also in the capacity for absorbing shock in virtue of the hysteresis effects associated with repeated stressing. A general discussion follows the paper. C. C. DAVIS

The long spacings of rubber and cellulose. GEO. L. CLARK AND KENNETH E. CORRIGAN. *Rubber Chemistry & Technology* **4**, 213–8(1931).—See *C. A.* **24**, 5180. C. C. DAVIS

Utilization of waste rubber. E. B. BUSENBURG. *Trans. Inst. Chem. Eng.* Dec., **1930**, 56–8.—A review. B. C. A.

Isoprene and rubber. XX. The colloidal nature of rubber, gutta-percha and balata. H. STAUDINGER. *Rubber Chemistry & Technology* **3**, 586–95(1930).—See *C. A.* **24**, 4655. **XXI. The molecular size of rubber and the nature of its colloidal solutions.** *Ibid* 596–603.—See *C. A.* **24**, 4954. **XXII. Isorubber nitrone.** H. STAUDINGER AND H. JOSEPH. *Ibid* **4**, 191–200(1931).—See *C. A.* **25**, 2591. **XXIII. Cryoscopic measurements of rubber solutions.** H. STAUDINGER AND H. F. BONDY. *Ibid* 201–5.—See *C. A.* **25**, 2592. **XXIV. Reduction of rubber with hydriodic acid.** H. STAUDINGER AND JAMES R. SENIOR. *Helv. Chim. Acta* **13**, 1321–4(1930); cf. *C. A.* **25**, 2591–2.—Hydrogenation of rubber with P and HI causes a partial cracking and cyclicization of the rubber mol., which is more marked at higher reduction temps. Completely satd. hydrocarbons were obtained in runs at 245–50° and 280°. The mean mol. wts. (in camphor) of these prepns. were 1200 and 1700, resp. Neither could be distd. without decompn. (cf. Berthelot, *Bull. soc. chim.* [2], **11**, 33(1869)). Analysis of each showed C 1% above and H 1% below calcd. values for C_5H_{10}. **XXV. Polymeric homologs of hydrorubber.** H. STAUDINGER. *Ibid* 1324–34.—The hydrorubbers prepd. by various procedures are considered as a homologous series, such as that formed by the polystyrenes, and similarities are pointed out. Elasticity in a substance of high mol. wt. is thought to be dependent on its mol. length. The soly. of hydrorubbers is much greater than that of *n*-paraffins of high mol. wt., but S. believes this is due to the side chains in hydrorubber. Hydrobutadiene rubber is sol. and probably has a branched structure. **XXVI. Hemicolloidal hydrorubbers.** H. STAUDINGER, E. GEIGER, E. HUBER, W. SCHAAL AND A. SCHWALBACH. *Ibid* 1334–49.—If rubber is heated (without solvent) and at the same time very rapidly hydrogenated, hemicolloidal hydrorubber results. The hydrogenation rate with various catalysts was studied at 275–80° under 100 atm. pressure. The app. of S. and Fritschi (*C. A.* **17**, 2974) was used. Samples were prepd. by mixing the catalyst and rubber in concd. C_6H_6 soln., pptg. with EtOH and removing the solvents. Ni, Co, Pt, Fe and Cu catalysts were used; Co or Ni on pumice was best and a 1:1 ratio of rubber to catalyst was most effective. Uncyclicized hydrorubbers were obtained with Co, Ni and Pt catalysts. Mol.-wt. detns. on these samples by f.-p. depression in C_6H_6 and by viscosity measurements agreed well and gave values from 1600 to 10,000. The sample prepd. with Co had n_D^{16} 1.4768, d_4^{15} 0.8585, and decompd. above 330°. Purified rubber (mol. wt. 70,000 by viscosity measurements) when swelled with cyclohexane and hydrogenated similarly gave hydrorubber of mol. wt. 16,000 by viscosity measurements. The mol. wt. of this sample detd. cryoscopically in cyclohexane or camphor was variable (3000–6000). Similarly, purified gutta-percha, when alone and when swelled with cyclohexane, was hydrogenated to products with mol. wts. (by viscosity measurements) of 5500 and 14,000, resp.; purified balata behaved analogously. Measurements of *n* indicate that hydrorubber, hydrogutta-percha and hydrobalata are identical. **XXVII. The relation between viscosity and molecular weight of hydrorubbers.** H. STAUDINGER AND R. NODZU. *Ibid* 1350–4.—The const. K_m in the formula $K_m = \eta_{sp.}/(cM)$ (cf. *C. A.* **24**, 3131, 5717) has been detd. for hydrorubbers. Com. hydrorubbers (prepd. by relatively slow hydrogenation and hence much cyclicized) gave for K_m 7.5–20 $\times 10^{-4}$ according to whether the samples were prepd. at 300–40° or 240–5°, and the mol. wts. of these samples detd. cryoscopically were 0.5–0.25 of those found by the formula above. Hydrorubbers prepd. by rapid hydrogenation gave for K_m 2.6–3.4 $\times 10^{-4}$, and mol. wts. cryoscopically detd. were not widely different. Since K_m for rubber is about 3 $\times 10^{-4}$, the length of the mol. rather than solvation at its double bonds governs its viscosity. **XXVIII. Fractionation and cracking of hydrorubber.** H. STAUDINGER AND W. SCHAAL. *Ibid* 1355–60.—Hydrorubber consists of a mixt. of homologous polymers. A hydrorubber (mol. wt. 14,000) when fractionally pptd. from Et_2O soln. by EtOH gave fractions ranging in mol. wt. from 5000 to 21,000. Mol. wts. were detd. from viscosity measurements. Hydrorubbers prepd. by the exact method of Pummerer and Koch (*C. A.* **18**, 3737) and by high-temp. hydrogenation had $\eta_{sp.}/c$ 6.1 and 3.9, resp. Distn. of these in an abs. vacuum gave distillates having

$\eta_{sp.}/c$ 0.5 and 0.3, resp. The distillate from the hydrorubber prepd. at high temp. was fractioned; no satd. substance was isolated. **XXIX. Hydrorubbers of high molecular weight.** H. STAUDINGER AND W. FEISST. *Ibid* 1361–7.—Sol rubber (mol. wt. 45,000) hydrogenated in 0.9% methylcyclohexane soln. with Pt gave hydrorubber of mol. wt. 31,000. Gel rubber of mol. wt. 70,000 (0.68% in methylcyclohexane) hydrogenated at 180–200° and 100 atms. gave hydrorubber of mol. wt. at least 32,000. Mol. wts. were detd. by viscosity measurements. It is shown that, in contrast to rubber, the relative viscosity of these hydrorubber solns. does not change with temp. This hydrorubber tends to assoc. in concd. soln., as do the polystyrols; in solid form it is slightly elastic. **XXX. Hydromethylrubber.** H. STAUDINGER, M. BRUNNER AND E. GEIGER. *Ibid* 1368–74.—High-temp. hydrogenation of methylrubber breaks down the mol. more completely than in the case of rubber. At 270–80° and 100 atm. pressure with 2.5% of Pt catalyst the product is a mixt. The mixt. is only partially pptd. from Et_2O by EtOH; from the sol. portion was isolated a *substance* $b_{0.13}$ 50–70°, n_D^{20} 1.45747, d_4^{15} 0.8318, which had a mol. wt. of 168 and analyzed $C_{12}H_{24}$. Fractional pptn. of the EtOH-insol. material from Et_2O gave a fraction of mean mol. wt. 1000, with the compn. $(C_6H_{12})_x$. Hydrogenation of methylrubber with an equal quantity of Ni catalyst at 260–70° and 90 atm. gave a *hydromethylrubber* of mol. wt. 1550, d_4^{16} 0.8770 and n_D^{16} 1.4844. This product resembles hydrorubber chemically and physically except that it is less viscous: viscosity measurements gave the const. K_m 4.4×10^{-4}. **XXXI. The polymerization of isobutylene.** H. STAUDINGER AND M. BRUNNER. *Ibid* 1375–9.—$CH_2:CMe_2$ was polymerized over Florida earth (Lebedev and Filonenko, *C. A.* **19**, 1555) and a mixt. of the polymers of highest mol. wt. was sepd. by pptn. from Et_2O by EtOH. This mixt. was a viscous mass which had d_4^{17} 0.9007, n_D^{17} 1.5022 and a mean mol. wt. 1600 (detd. cryoscopically in C_6H_6). It was stable to warm $KMnO_4$ or HNO_3; Br added to about 50% of the theory for $(C_4H_8)_{26} + 1\Delta$, and viscosity detns. gave the const. K_m 1.78×10^{-4}. The soly. was exactly similar to hydrorubber. This indicates that a branched-chain paraffin of high mol. wt., like hydrorubber, need not be so insol. as the analogy with *n*-paraffins suggests. A. F. SHEPARD

A study of gutta-percha and balata by means of x-ray spectra. H. HOPFF AND G. VON SUSICH. *Rubber Chemistry & Technology* **4**, 75–81(1931).—See *C. A.* **25**, 434. C. C. DAVIS

Some notes on ebonite. H. RIDING. *Trans. Inst. Rubber Ind.* **6**, 230–47(1931).—A review and discussion of the historical aspects of the manuf. of hard rubber, the properties of com. types, the present trend in testing methods, with crit. comments on recently published works and with some new data obtained by R. The new expts. are closely related to those of Perks on the thermochemistry of the rubber-S reaction (cf. *C. A.* **20**, 2595). Samples from a base mixt. of rubber 65, S 35, with and without diphenylguanidine, hard-rubber dust and amorphous Si in various combinations, were cured in such a way that the internal temp. could be measured as the vulcanization progressed. The results, which are shown in graphical form, show that: (1) the exothermic reaction began at the same relative state of cure with all the mixts., *viz.*, at a vulcanization coeff. of approx. 8, and (2) the velocity of the reaction is a function of the rate of vulcanization, *i. e.*, the rate of combination of rubber and S, whether governed by the temp. of vulcanization, by accelerator or by both. Between vulcanization coeffs. of 8 and 40, the rubber-S addn. reaction is exothermic. The rate of combination of rubber and S is more rapid in an accelerated mixt. than in a non-accelerated one, and the g.-cals. generated per unit time are therefore greater. However, the rate of diffusion of heat in the unit masses of the mixt. is the same, and therefore the resultant temp. in an accelerated mixt. is higher than in the corresponding unaccelerated mixt. It is probable that the quantity of heat generated per unit mass of new rubber is const., as long as there is sufficient S to complete the reaction. Hard-rubber dust acts merely as a diluent, and this was confirmed in the mixt. contg. SiO_2, which gave results almost identical with the corresponding mixt. contg. hard-rubber dust. A reduction in the proportion of uncombined rubber-S mixt. by addn. of hard-rubber dust to the mixt. results in a diminution in the total quantity of heat generated. With other conditions the same, the extent of diln. and the diffusivity const. govern the temp. rise. When the thickness of the sample is such that the rate of heat generation exceeds the rate of heat diffusion, the velocity of the reaction increases because of the rise in temp., and the effect is more marked. It is necessary, therefore, to regulate the velocity of the reaction so that it is equaled or exceeded by the rate of diffusion, which may be done by: (1) reducing the rate of vulcanization by lowering the temp. of vulcanization or eliminating accelerators, or (2) using a diluent like hard-rubber dust. The expts. do not agree with the common idea that hard rubber dust retards the rate of vulcanization, for the slower

curing rate was due to the smaller evolution of heat from sheets of a thickness such that at a certain temp. the diffusivity equaled the heat of reaction, and a true temp. level resulted. A general discussion follows the paper. C. C. DAVIS

The influence of zinc oxide on the action of the principal accelerators of vulcanization. R. THIOLLET AND G. MARTIN. *Rubber Chemistry & Technology* **4**, 1–7(1931).—See *C. A.* **24**, 5179. C. C. DAVIS

The influence of rubber "resins" in zinc oxide-accelerator mixings. W. S. DAVEY. *Rubber Chemistry & Technology* **4**, 156–63(1931).—See *C. A.* **24**, 5534. C. C. DAVIS

Studies of the conditions affecting the vulcanization of rubber. V. The effect of accelerators on the heat of vulcanization. Y. TOYABE. *Rubber Chemistry & Technology* **4**, 190(1931).—See *C. A.* **25**, 1118. C. C. DAVIS

The kinetics of the vulcanization of rubber. BIRGER W. NORDLANDER. *Rubber Chemistry & Technology* **4**, 164–89(1931).—See *C. A.* **24**, 5535. C. C. DAVIS

Overflow during vulcanization, its dependence upon inactive and active fillers and errors in previous calculations of the specific gravity of vulcanizates resulting from it. RUDOLF DITMAR AND CARL H. PREUSSE. *Rubber Chemistry & Technology* **4**, 24–8 (1931).—See *C. A.* **24**, 5179–80. C. C. DAVIS

Vulcanization of rubber with trinitrobenzene. BUREAU OF STANDARDS. *J. Franklin Inst.* **210**, 664–5(1930); *Caoutchouc & gutta-percha* **28**, 15360(1931).—Unlike S vulcanizates, rubber vulcanized with 1,3,5-$C_6H_3(NO_2)_3$ does not tarnish Cu, Ag, Ni, Fe and Hg, and rubber may also be vulcanized in contact with Cu without loss of luster by the Cu and without detriment to the subsequent aging of the rubber. This means that rubber cured with 1,3,5-$C_6H_3(NO_2)_3$ can be utilized for elec. insulation in conjunction with Cu. The mixt.: pale crepe 100, 1,3,5-$C_6H_3(NO_2)_3$ 2, ZnO 100, cured 60 min. at 141°, had a dielec. const. 3.84, a power factor of 0.006 (1000 cycles, 27°) and a resistivity of 1.4×10^{16} ohms per cm. C. C. DAVIS

Effect on vulcanized rubber compounds of immersion in boiling water. K. J. SOULE. *Ind. Eng. Chem.* **23**, 654–8(1931).—After proving in preliminary expts. that there is a great difference in the rate of water absorption by vulcanizates of different types, systematic expts. were carried out by adding to the base mixt.: smoked sheet 100, S 3, diphenylguanidine 1, ZnO 9, equal vols. of 36 different powders and detg. the time-swelling curves of the optimum vulcanizates in boiling water. In all cases swelling was at first rapid and then relatively slow, and was thus similar to the effect in org. liquids (cf. Scott, *C. A.* **24**, 4664). With some of the fillers, the swelling was less than with the base vulcanizate, but the majority of the fillers increased the rate and extent of swelling. The vulcanizate contg. C black swelled the least, that with ultramarine blue the most. A parallel test with uncured smoked sheet showed far greater swelling, but no disintegration after 1000 hrs. There was no simple relation between the proportion of water absorbed and the resistance to cutting, though in general the smaller the quantity of water absorbed, the greater the resistance. Neither was there any simple relation between swelling and hardness. C. C. DAVIS

Tensile tests of vulcanized rubber at high speed. A. VAN ROSSEM AND H. B. BEVERDAM. *Rubber Chemistry & Technology* **4**, 147–55(1931).—See *C. A.* **25**, 2595. C. C. DAVIS

A guide to the literature on rubber. ANON. Bur. Standards, *Letter Circ.* **305**, 15 pp.(1931). E. H.

Rate of deposition of latex on porous molds. H. W. GREENUP. *Ind. Eng. Chem.* **23**, 688–91(1931).—Expts. show the effects of the pressure, temp., concn. of the rubber in the latex and the H-ion concn. upon the rate of deposition from latex on porous molds. The pressure, temp. and concn. played an almost negligible part compared with the H-ion concn. By adjusting the p_H of the latex to 6.1, it was possible to aggregate the latex particles and increase considerably the rate of deposition. C. C. DAVIS

A comparison of stearic and sebacic acids as rubber softening agents. KATSUMI ISHIGURO. *J. Rubber Soc. Japan* **2**, 238–42(1930).—In general, stearic acid showed the best softening action on rubber, but sebacic acid gave the best softening action when it was used in excess with ZnO. With an increase in ZnO, sebacic acid improved the quality of vulcanized rubber greatly, and it did not retard the action of vulcanization accelerators. It is comparatively safe to use as an anti-aging agent for vulcanized rubber. It is suggested that sebacic acid be studied more as a vulcanization accelerator than as a softening agent. K. KITSUTA

An instrument for testing the hardness and permanent set of rubber, and for measuring the thickness of test pieces. H. A. DAYNES, E. B. JOHNSON AND J. R. SCOTT. *Trans. Inst. Rubber Ind.* **6**, 63–81(1930).—The new instrument, which is described and illustrated, makes possible a hardness detn. in 1 operation, by a direct measurement of the indentation relative to the original unloaded surface of the rubber.

The reference plane which makes contact with the rubber surface is a flat surface of comparatively large area, resting on the rubber surface which immediately surrounds the point of application of the indenting knob. This construction avoids certain disadvantages of the static indentation type, which are discussed in detail. By an auxiliary attachment this new instrument may also be utilized for measuring the thickness of rings at 3 points simultaneously. A simple app. for measuring the permanent set of ring test-pieces is also described and illustrated. C. C. DAVIS

Effect of storage on milled crude rubber. C. M. CARSON. *Ind. Eng. Chem.* **23,** 691–4(1931).—Smoked sheet was milled to different degrees of plasticity and was then compressed in bales and stored at 10–20° and at 55° for various periods up to 9 months. The plasticity and the resiliency (recovery after the plasticity detn.) of the uncured rubber, and the stiffness (modulus) after curing were measured periodically, so that the progressive changes in these properties could be ascertained. The effect of storage was manifest to the greatest extent in the recovery values, which under all conditions increased progressively throughout, with the greatest increases at 10–20°. Rubber baled at 43° showed greater recovery during storage than that baled at 100°. The modulus values also increased considerably, with the greatest increases in the rubber stored at 55°. The plasticity values increased relatively little, with the greatest increases at 10–20°. With increasing time of storage, there was a tendency for the rate of vulcanization to increase. In typical factory mixts. the aged rubber caused greater roughness and slower extrusion than did the freshly milled rubber. The extrusion type of plastometer is a much better criterion than the compression type for judging the extruding properties of a rubber mixt. Vulcanizates contg. the aged rubber aged more poorly, both in an O and in a N bomb test, than did those contg. fresh rubber, probably because the natural antioxidant disappeared during storage. During storage the acetone and acid no. diminished (perhaps because of polymerization of fatty acids), and the alc. KOH ext. and N in the acetone ext. increased, so that the first 2 chem. changes were the opposite of those when rubber is heated. When chilled, milled rubber "freezes" below 0° and thaws at 15–30°, but it also "freezes" when maintained under slight pressure for several months at 5–35°, and when either sheet or milled rubber is hardened by this latter method, it does not soften until heated to 50°. C. C. DAVIS

Value of zinc sulfide as a rubber compound. KYOICHI NAMITA. *J. Rubber Soc. Japan* **2,** 157–9(1930).—To a base mixt. which consisted of 93.5% rubber and 6.5% S, 2, 5, 15 and 30% by vol. of ZnS and ZnO, resp., were added. Detns. of tensile strength, elec. insulating power and whiteness of the finished products showed a superiority in the rubber compounded with ZnS over that with ZnO. In comparing ZnS and ZnO as vulcanization accelerators, no differences were found up to 3.5 hrs., but from this point, acceleration was much greater with ZnS than with ZnO. From the acetone ext., it is concluded that the acceleration was much greater with ZnS from the beginning. K. KITSUTA

A new process for the preparation of sheet rubber. N. H. VAN HARPEN. *Arch. Rubbercultuur* **14,** 425–36(1930) (in English 437–48); *Chem. Zentr.* **1931,** I, 1977.—The time of drying is proportional to the square of the thickness of the sheets, and therefore by making the sheets only 0.5 as thick, 75% of the smoking and drying time can be saved. The details of the production and the com. merits of such thin sheet are described. Data on costs are also included. C. C. DAVIS

The plasticization of rubber. F. JACOBS. *Rev. gén. caoutchouc* **8,** No. 70, 15–24 (1931); cf. *C. A.* **25,** 2875.—Recent exptl. developments by various investigators on the use of stearic acid in rubber compounding are reviewed and discussed. C. C. D.

The stress-strain curves of rubber-carbon black mixtures at low temperatures. M. KRÖGER AND WAN-NIEN YAO. *Gummi-Ztg.* **43,** 649(1930); *Chem. Zentr.* **1931,** I, 171.—The expts. were to det. whether C black in rubber (Congo, Para, sheet) changed the stress-strain curves of the unvulcanized mixts. as it does of vulcanized rubber (cf. *C. A.* **23,** 4594). This was found to be true. The optimum energy was at approx. —25°. At lower temps. higher tensile strengths were found, but enough lower elongations so that the energy was lower. Compared with pure rubber, the optima were at higher temps. C. C. DAVIS

The refining of mineral black and its reënforcing and other properties. PHILIP SCHIDROWITZ AND MAURICE PHILPOTT. *Trans. Inst. Rubber Ind.* **6,** 96–116(1930); cf. *C. A.* **25,** 232.—The present paper describes a new method for refining crude Bideford mineral black (cf. Langton, *C. A.* **22,** 4260), and gives the results of expts. on its behavior in 2 types of exptl. vulcanizates: (1) rubber 100, S 5, PbO 30, black 0–80 and (2) rubber 100, S 4, diphenylguanidine 1, ZnO 10, black 36, which were given different cures. Their stress-strain curves and their aging properties (70° air oven) were detd., and the results compared with corresponding vulcanizates contg. different gas blacks

and lamp blacks, resp. Besides these, tests of the comparative effects on the tensile strength, resistance to tear and aging, of Bideford black and other blacks in 7 typical tire-tread mixts., a shoe mixt. and a sole mixt. were made. The results show that refined Bideford black has a greater reënforcing power than lamp black, and about 40% that of gas black. Unlike gas black, it does not retard the rate of vulcanization. Vulcanizates contg. Bideford black age satisfactorily; in fact the black tends to have a slight preservative effect. In general, Bideford black can replace all of the lamp black and up to about 25% of the gas black in certain important types of mixts. C. C. D.

Organic dyes in the rubber industry. F. JACOBS. *Kautschuk* **7**, 22–6(1931); *Chimie & Industry* **Special No.**, 672–82 (March, 1931).—A review and discussion, with a descriptive list of 93 English, French, German and American rubber dyes, including their characteristics in vulcanized rubber mixts. C. C. DAVIS

White pigments. F. HARRISS COTTON. *India Rubber J.* **81**, 675–6, 711–2(1931).—A review and discussion, with numerous references on lithopone and Ti white. C. C. DAVIS

Rubber for electrical uses. A. R. DUNTON AND A. W. MUIR. *Electrician* **106**, 679–81(1931).—A review and discussion with representative tests of special varieties of hard-rubber sheet. W. H. BOYNTON

Rubber grinding wheels. JOSEPH ROSSMAN. *India Rubber World* **84**, No. 3, 63–5(1931).—A review, with descriptions of numerous patents. C. C. DAVIS

Abrasion testing of rubber with Bureau of Standards type machine. WARREN E. GLANCY. *Proc. Am. Soc. Testing Materials* (preprint) **83**, 38–43(1931).—A modified form of the machine described by Sigler and Holt (cf. *C. A.* **25**, 842) is described and illustrated. Exptl. data obtained with this machine on vulcanized tire tread, heel, sole and exptl. mixts. show a good agreement between the lab. and service tests, and also between the cures at which the resistances to abrasion were highest and those at which the tensile strengths were highest. C. C. DAVIS

Abrasion tests of vulcanized rubber compounds, using an angle abrasion machine. J. L. TRONSON AND A. W. CARPENTER. *Proc. Am. Soc. Testing Materials* (preprint) **83**, 16–30(1931).—The new machine, which is described and illustrated, is similar to that of Vogt (cf. *C. A.* **22**, 1500). With it the effect of variations in load, speed, temp., size of test sample, methods of processing the uncured mixts., state of cure and accelerated aging on the resistance to abrasion of several tread mixts. were studied, and also the relative abrasion values were compared with road tests. Judged by this machine, resistance to wear depended upon the method of mixing and upon the degree of dispersion of the fillers. It diminished progressively with overcure and with artificial aging (70° oven), and the low values obtained with undercured mixts. bore no relation to the results of road wear. However, at the proper cures, the method is a good criterion of the behavior of the road, and is of value in exptl. development, in place of service tests. C. C. DAVIS

Comparative tests of four abrasion machines. C. A. KLAMAN. *Proc. Am. Soc. Testing Materials* (preprint) **83**, 44–9(1931).—Tests with the du Pont machine (cf. Williams *C. A.* **21**, 2573), the Kelly machine (cf. Hardman, Mackinnon and Jones, *C. A.* **25**, 1705), the U. S. Rubber Co. machine (cf. R. T. Vanderbilt Co. Handbook, 72) and the N. J. Zinc Co. machine (cf. Depew, *C. A.* **22**, 3064) agreed with road service tests in a satisfactory way when vulcanizates were cured to the optimum state, but did not agree with the service tests when the mixts. were under- or overcured. Consequently none of the machines are suitable for specification testing, and they are reliable only for lab. investigations where the state of cure is controlled. Results could be reproduced satisfactorily on any of the machines. C. C. DAVIS

Shock-absorbing properties of rubber. MATSUO SHIMATANI. *J. Rubber Soc. Japan* **2**, 243–50(1930).—By use of a special app., a curve of decrement in motion is proved experimentally to be expressed by the formula: $y = b.e^{-\lambda t}$, where y is a function of time t, b and λ are constants and e is the base of natural logs. λ represents the logarithmic decrement. K. KITSUTA

The [rubber] reclaiming industry in the United States. L. P. MAX. *Rev. gén. caoutchouc* **8**, No. 70, 7–13(1931).—A general review and discussion. C. C. DAVIS

Recovery of rubber and cotton from uncured tire-ply scrap. Extraction process. CHARLES S. POWELL. *Ind. Eng. Chem.* **23**, 701–3(1931).—A new method of reclaiming uncured tire-ply scrap, which is an application of the solvent-extn. process with C_6H_6 as solvent, is described and illustrated. This new process possesses several advantages over previous methods of sepg. rubber and fabric in scrap, particularly on the basis of waste, for both the cotton and the rubber are completely reclaimed without detriment to quality. The cotton contains about 1% rubber, and may be utilized in the *manuf. of paper*, as a filler for cheap felt, or when ground as cotton floc. To make the new

process of more general application, a use for the dil. (6%) rubber cement formed must be found. C. C. DAVIS

Vultex. Characteristics and rubber-manufacturing applications of vulcanized latex. VULTEX CHEMICAL CO. *India Rubber World* **84**, No. 3, 58(1931).—Descriptive. C. C. DAVIS

Isoprene and rubber. XXXII. The constitution of rubber. H. STAUDINGER. *Kolloid-Z.* **54**, 129–40(1931); cf. *C. A.* **25**, 3518–9.—The detn. of mol. wt. by the detn. of the end groups as suggested by Pummerer (cf. *C. A.* **25**, 1410) is applicable to hemicolloids with mol. wts. from 1000 to 10,000. It is not exact for the mol.-wt. detn. of rubber because of the difficulty of properly distinguishing end groups with analytical reactions and because of the large errors involved in the detn. of a small percentage of end groups in substances of high mol. wt. The detn. of mol. wt. by viscosity measurements, the swelling of rubber and stability of macromolecules are reviewed. A. F.

A method of making electrical contact with ebonite and soft rubber for insulation tests. H. F. CHURCH AND H. A. DAYNES. *Trans. Inst. Rubber Ind.* **6**, 82–95(1930).—Expts. show that the dried coating of graphite remaining after evapn. of the water from "Aquadag" (a com. product composed of a colloidal aq. suspension of graphite stabilized with NH_3) forms a convenient electrode for elec. measurements under a variety of conditions. The apparent vol. resistivity of a sample of hard rubber (resistivity above 10^{16} ohms per cc.) was greater with 1 graphite and 1 Hg electrode than with 2 graphite electrodes, and this difference is attributed to a considerable resistance of contact between Hg and hard rubber. The actual contact resistances between hard rubber and graphite or Hg were not measured. Provided that measurements are not taken too soon (a few hrs.) after application of the graphite suspension, the aq. medium is not objectionable in detns. of vol. and surface resistivities of soft rubber and of hard rubber. This agrees with closely related expts. by other investigators (cf. *J. Inst. Elec. Eng.* **67**, 271(1929)), and the high contact resistances support the theory that the resistance depends upon contact with the insulator only in parts, so that there is constriction of lines of flow and crowding of equipotential surfaces near the face where contact occurs. The method should be useful with many materials other than rubber. The expts. were confined to d. c., but should be satisfactory for a. c. A general discussion follows the paper. C. C. DAVIS

The fluorescence of organic vulcanization accelerators. KITARO KOJIMA AND IZUMI NAGAI. *J. Rubber Soc. Japan* **2**, 260–2(1930); cf. *C. A.* **23**, 3408.—After exposure to ultra-violet light from a quartz-Hg lamp, most of the org. vulcanizing agents produced a characteristic fluorescence, which in some cases is of value for identification. Fluorescent colors of 41 different vulcanization accelerators were tested, H_2O, EtOH, C_6H_6 and CCl_4 being used as solvents. K. KITSUTA

Accelerators of vulcanization. F. JACOBS. *Caoutchouc & gutta-percha* **28**, 15522–5 (1931); cf. *C. A.* **25**, 3198.—The properties and behavior of the com. accelerators, "Altax" and "Vulkacit D. M." are described. C. C. DAVIS

Studies on the thermochemistry of rubber. I. Heat of vulcanization of rubber. KYOICHI NAMITA, KOICHI FUKAYA AND TAKEJI NAKAJIMA. *J. Rubber Soc. Japan* **2**, 389–97(1931).—The sample was prepd. by vulcanizing at 40–50 lbs. pressure for 2–15 hrs. Vulcanized samples were extd. with acetone and kept in acetone. The acetone was removed by vacuum-drying before the combustion expts. The samples thus prepd. contained no free S. The heat of vulcanization was calcd. from the following equation: $Q = Q_1 + aQ_2 + bQ_3 + c(Q_4 + Q_5)$, where Q = heat of vulcanization, Q_1 = heat of combustion of sample, aQ_2 = heat of combustion of compounded rubber, bQ_3 = heat of combustion of combined S (all corrections for heat of formation and soln. of H_2SO_4 were made), cQ_4 = heat of combustion of protein in sample, cQ_5 = heat of reaction between protein and S. a, b and c are the wts. of pure rubber, S and protein, resp., in 1 g. of sample. The signs of Q_2, Q_3 and Q_4 are pos., while Q_1 and Q_5 are neg. The results showed that the vulcanization of soft rubber up to 4% combined-S content is an endothermic reaction, but that from this point, the reaction changes to exothermic, reaching its max. value at 12% combined-S content, then gradually decreasing as the combined-S increases up to 22%, where it forms hard rubber. With increase in combined S above 22%, the reaction changes to endothermic. This result is quite different from that of Blake (cf. *C. A.* **24**, 4424), and the difference may be attributed to the higher content of resinous substance in his sample. K. KITSUTA

Studies on the heat of reaction during the vulcanization of rubber. YASUSHI TOYABE. *J. Rubber Soc. Japan* **2**, 251–4(1930); cf. *C. A.* **25**, 1118.—The app. used for this expt. consisted of a glass desiccator, which was large enough to contain a small elec. furnace, in which stood 2 small test tubes, one contg. the sample and the other asbestos fiber. An elec. thermocouple was inserted in each tube, and both were con-

nected by wire to the galvanometer. The results showed that the heat of reaction during the vulcanization gradually increased to a max. value in about 1 hr., and then gradually decreased to the temp. of the heating medium. However, with the addn. of vulcanizing accelerators, the max. heat of vulcanization was reached immediately, and then it decreased. Analysis of the sample when it reached the point of max. heat of vulcanization showed approx. 50% of S combined with rubber, and this ratio could not be changed by changing the temp. of vulcanization, nor by differences in compounding of the rubber. These facts suggest that there occurred a great change in the state of aggregation of the hydrocarbon of the rubber mol. by the addn. of accelerators. K. K.

Effect of rubber compounding on the specific gravity of vulcanized rubber. KYOICHI NAMITA, TAKEJI NAKAJIMA AND KINZO TSUTSUNI. *J. Rubber Soc. Japan* **2**, 408–13(1931).—The following addnl. formula generally in use for the estn. of the d. of vulcanized rubber gave ±0.04 errors: d. of rubber = $100/[(a/P_a) + (b/P_b) + (c/P_c) - - - - + (n/P_n)]$, where $a, b, c, - - - n$ are the % of each ingredient, and $P_a, P_b, P_c - - - - P_n$ are the d. of each ingredient. Better agreement was obtained by the use of either one of the following formulas: $y = 0.95 + mx$, where y = d. of the compounded rubber, x = % by vol. of substance used for rubber compounding, m = const. corresponding to the slope of a curve obtained by plotting x as abscissa and d. of compounded rubber as ordinate. Or $y = 0.95\ (x + 1)^b$, where y = d. of compounded rubber, x = % by wt. of substance used for rubber compounding, b = const. corresponding to the slope of a curve obtained by plotting x as abscissa and d. of compounded rubber as ordinate. The d. of vulcanized rubber was calcd. as 0.95 in this case. K. KITSUTA

Estimation of carbon black in vulcanized rubber. KYOICHI NAMITA. *J. Rubber Soc. Japan* **2**, 255–60(1930); cf. *J. Rubber Soc. Japan* **1**, 62.—The method of Ooyaji consists in placing 2 g. of sample in a Rose crucible, covering, and passing N for 2 min. at the rate of 2 bubbles per sec., then heating over a Bunsen burner for 4 min., removing the burner and cooling the crucible while passing N. The crucible was then placed in a desiccator and weighed. The calcn. of C was as follows: $B = [F - \Sigma(1 - Fu) \cdot Du]/-(1 - K)$, where B = % C, F = wt. of residue after combustion in N, Fu = a const. for each ingredient, Du = % of each ingredient, K = const. for C. Values for Fu are as follows: rubber = 100/100, $CaCO_3$ = 0.2/100, ZnO = 0.56/100, black salve = 98.2/100, lithopone = 0.85/100, C = 2.2/100, clay = 1.9/100, S = 100/100, $MgCO_3$ = 54.5/100, vegetable oils = 100/100, MgO = 0.9/100, mineral rubber = 81/100, $Ca(OH)_2$ = 12.8/100, PbO = 1.0/100. The above formula is of sufficient accuracy for the quant. recovery of the added C, except when the sample contains $CaCO_3$, which makes the result too low. This is due to the dissocn. of CO_2 from $CaCO_3$ on heating in N. The reaction between CO_2 and C take place as follows: $C + CO_2 \longrightarrow 2CO$. The CO produced is lost as gas; therefore, this method is not reliable when the sample contains carbonates which give off CO_2 on heating. K. KITSUTA

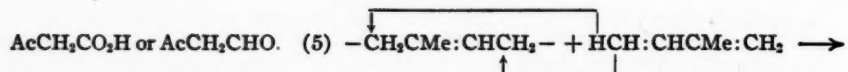
Vulcanizing experiment with various carbon blacks. KATSUMI ISHIGURO, KENPAKU FUJIKI AND HARUO ISHIGURO. *J. Rubber Soc. Japan* **2**, 403–8(1931).—No definite relations were found between the particle size and the O content of C black and the mech. strength of rubber compounded with it. K. KITSUTA

The estimation of chloroform-soluble substances of vulcanized rubber without added organic ingredients. IWASABURO MINATANI AND ICHIRO AOE. *J. Rubber Soc. Japan* **2**, 235–8(1930).—The sample was prepd. from 100 parts of raw rubber, 100 parts of $BaSO_4$, 5 parts of S and 10 parts of MgO. During the vulcanization (20 min. to 5 hrs.), samples were taken for extn. of the acetone ext., $CHCl_3$ ext., free S content and C and H of the $CHCl_3$-sol. portion. The analyses showed that the acetone ext. and free S content decreased as the time of vulcanization increased, without exception, but that the $CHCl_3$ ext. decreased up to 1⅔ hrs., then it had a tendency to increase. Analysis of the $CHCl_3$-sol. substance from the vulcanized material cured 20 min. was found to be pure undecomposed rubber $(C_5H_8)x$, but an excessively long vulcanization caused decompn. of a part of rubber into some resinous substance. This explains why the $CHCl_3$-sol. substance increased after 1⅔ hrs. K. KITSUTA

Study of a test for tear resistance of vulcanized rubber compounds. A. W. CARPENTER AND Z. E. SARGISSON. *Proc. Am. Soc. Testing Materials* (preprint) **83**, 5–15 (1931).—A study was made of (1) the extent to which resistance to tear depends upon grain; (2) the extent to which resistance to tear depends upon the state of cure; (3) the effect of changing the curvature of the test piece on the resistance to tear; and (4) the relation between resistance to tear and compn. and to resistance to abrasion and stress-strain properties. The original Goodrich method in modified form was used, the details of which are described and illustrated. The results show that resistance to tear by this method is not influenced by the direction of testing, probably because the tear always follows the grain, so that the tearing force is that required to sep. the

fibrous structure and not to rupture the fibers. Resistance to tear is a function of the state of cure, and passes through a max. near the "optimum" cure (based on stress-strain properties). A small change in the curvature of the sample has no practical effect. Resistance to tear is increased by the addn. of C black or ZnO to a rubber mixt. and is diminished by the addn. of whole tire reclaim. Among a series of vulcanizates of differing compn., there was a rough parallelism among the resistance to tear, the resistance to abrasion and the tensile strength. C. C. DAVIS

Some fundamental rubber problems. G. STAFFORD WHITBY. *Trans. Inst. Rubber Industry* **5**, 184–95(1929); **6**, 40–62(1930).—A crit. review and discussion, with new points of view and new data, dealing with (1) the chem. constitution of rubber (I) in its relation to the mechanism of polymerization in general, (2) the phys. structure of I in its relation to the behavior of artificial elastic colloids and (3) the nature of vulcanization in its relation to the vulcanization of fatty oils. The wt. of evidence on the nature of polymerization favors the idea that in I the polymeric condition is built up through primary valences. Auer (cf. *C. A.* **23**, 4370) has attempted to prove that metastyrene (II) is formed through colloidal forces and distyrene (III) by true polymerization through primary valences, but this is disproved by unpublished expts. of W. and Katz, where it was found that the pyrogenic decompn. of II *in vacuo* yields III and tristyrene. The mechanism of polymerization suggested by W. and K. (cf. *C. A.* **22**, 1972) is probably typical of unsatd. compds. which form high-mol. polymers, and in general it is characterized by successive addns. to the double bond of the monomer or of the previous polymeric compd. with the migration of a H atom to 1 side of the double bond and the residue to the other side. Each stage represents a definite chem. individual. Unpublished expts. show that when polyindenes are decompd. by heat *in vacuo*, the mol. chain splits at different points (as with II), and mono-, di-, tri- and tetraindene distil, leaving a residual mixt. of polyindenes with higher mol. wts. than tetraindene, but lower than the original substance. As with II, the larger the polyindene mol., the greater the ease of cracking. Because of accompanying cyclicization, the decompn. of I by heat is not so simple as that of polyindenes; nevertheless it is probable that the mechanism of polymerization of isoprene (IV) to I is similar to that of indene, in which case a formula of I in accord with exptl. evidence can be derived. Any scheme must lead to a very high polymer, which on ozonolysis yields preponderantly levulinic acid (V) and levulinaldehyde (VI). There are 6 possible polymerizations of $(x + 2)$ IV mols., 2 of which ((1) and (2) below) involve 1,2-addn. and 4 of which ((3) to (6) below) involve 1,4-addn. At each stage there is a conjugated system like that in the original IV, for all products are IV with a long-chain substituent. (1) $H_2C{:}CMeCH{:}CH_2 + HCH{:}CMeCH{:}CH_2 \longrightarrow H_2C{:}CMeCH_2CH_2CH{:}CMeCH{:}CH_2 \xrightarrow{+\ IV} H_2C{:}CMeCH_2CH_2CH{:}CMeCH_2CH_2CH{:}CMeCH{:}CH_2 \xrightarrow{+\ (x-1)\ IV} H_2C{:}CMeCH_2CH_2[CH{:}CMeCH_2CH_2]_xCH{:}CMeCH{:}CH_2$; ozonolysis to $(x + 1)$ mols. V or VI, 2 mols. HCO_2H (VII) and 1 mol. $AcCO_2H$ (VIII) or AcCHO (IX). (2) $H_2C{:}CHCMe{:}CH_2 + HCH{:}CMeCH{:}CH_2 \longrightarrow H_2C{:}CHCHMeCH_2CH{:}CMeCH{:}CH_2 \xrightarrow{+\ IV} H_2C{:}CHCHMeCH_2CH{:}CMeCH_2CH_2CH{:}CMeCH{:}CH_2 \xrightarrow{+\ (x-1)\ IV} H_2C{:}CHCHMeCH_2[CH{:}CMeCH_2CH_2]_xCH{:}CMeCH{:}CH_2$; ozonolysis to x mols. V or VI, 2 mols. VII, 1 mol. VIII or IX and 1 mol. pyrotartaric acid or aldehyde. (3) $-CH_2CMe{:}CHCH_2- + HCH{:}CMeCH{:}CH_2 \longrightarrow Me_2C{:}CHCH_2CH{:}CMeCH{:}CH_2 \xrightarrow{+\ x\ IV} Me_2C{:}CHCH_2[CH_2CMe{:}CHCH_2]_xCH{:}CMeCH{:}CH_2$; ozonolysis to x mols. V or VI, 1 mol. VII, 1 mol. VIII or IX, 1 mol. AcMe and 1 mol. malonic dialdehyde (X). (4) $-CH_2CH{:}CMeCH_2 + HCH{:}CHCMe{:}CH_2 \longrightarrow MeCH{:}CMeCH_2CH{:}CHCMe{:}CH_2 \xrightarrow{+\ x\ IV} MeCH{:}CMeCH_2[CH_2CH{:}CMeCH_2]_xCH{:}CHCMe{:}CH_2$; ozonolysis to x mols. V or VI, 1 mol. VII, 1 mol. VIII or IX, 1 mol. AcOH or AcH, and 1 mol.



$AcCH_2CO_2H$ or $AcCH_2CHO$. (5) $-CH_2CMe{:}CHCH_2- + HCH{:}CHCMe{:}CH_2 \longrightarrow$ $Me_2C{:}CHCH_2CH{:}CHCMe{:}CH_2 \xrightarrow{+\ IV} Me_2C{:}CHCH_2CH_2CH{:}CMeCH_2CH{:}CHCMe{:}CH_2 \xrightarrow{+\ (x-1)\ IV} Me_2C{:}CHCH_2CH_2CH{:}CMeCH_2[CH_2CH{:}CMeCH_2]_xCH{:}CHCMe{:}CH_2$; ozonolysis to $(x-1)$ mols. V or VI, 1 mol. VII, 1 mol. VIII or IX, 1 mol. succinic acid (XI) or aldehyde, and 1 mol. $AcCH_2CO_2H$ or $AcCH_2CHO$. (6) $-CH_2CH{:}CMeCH_2- + HCH{:}CMeCH{:}CH_2 \longrightarrow MeCH{:}CMeCH_2CH{:}CMeCH{:}CH_2 \xrightarrow{+\ IV} MeCH{:}CMeCH_2CH_2CMe{:}CHCH_2CH{:}CMeCH{:}CH_2 \xrightarrow{+(x-1)IV} MeCH{:}CMeCH_2CH_2CMe{:}CHCH_2[CH_2CMe{:}CHCH_2]_xCH{:}CMeCH{:}CH_2$; ozonolysis to $(x-1)$ mols. V or VI, 1 mol. VII, 1 mol. VIII or IX, 1 mol. AcH or AcOH, 1 mol. acetonylacetone, and 1 mol. X. Any of these is in accord with exptl. data provided x is very large, *i. e.*, where the no. of double bonds is too large to distinguish between n and $(n+1)$ bonds, for the schemes above require $(n+1)$ double bonds per n IV units, and H absorption. Br-addn. and mol.-refraction detns. have indicated 1 double bond per IV unit. The ozonolysis products in the schemes above are not incompatible with the numerous expts. of Harries. Of the 6 schemes, present knowledge does not make possible a definite choice. If the addn. of successive IV mols. proceeds with the max. regularity, *i. e.*, involves the same reaction, then a 1,2-addn. means scheme (1) and a 1,4-addn. scheme (3) or (4). On the contrary, the finding of XI as an ozonolysis product by Harries indicates scheme (5). The expts. of Lebeder on the catalytic hydrogenation of IV suggest that the addn. of 1 mol. of IV to another may proceed simultaneously according to schemes (1), (3) and (4), so that rubber is a mixt. of isomers, but the asymmetry of IV may restrict the addn. to 1 direction. Unpublished expts. by Farmer on the dipolar moment of alkyl-substituted butadienes may throw light on this. The problem might be settled by isolating the initial dimeric and trimeric products. Ostromuislenski (cf. *J. Russ. Phys.-Chem. Soc.* **47**, 1928(1915)) describes the dimer $H_2C{:}CMeCH_2CH_2{-}CH{:}CMeCH{:}CH_2$ from IV, but expts. (unpublished) by W. and Crozier, following the directions of O., failed to obtain this dimer. The $-CH_2CH{:}CMeCH_2[CH_2CH{:}CMeCH_2]_xCH_2CH{:}CMeCH_2-$ formula of Staudinger and Fritschi (cf. *C. A.* **17**, 2974) is so out of harmony with the principles of org. chemistry that it cannot be accepted. In spite of the evidence of Stevens (cf. *C. A.* **13**, 3039), it is generally believed that I consists of 2 parts of the same proximate compn. Some of the evidence in favor is not, however, convincing, *e. g.*, the expts. of Bruson, Sebrell and Calvert on the action of $SnCl_2$ on I (cf. *C. A.* **21**, 3486), where the solvent for sepg. the product was different from that for sepg. the original I. A long series of expts. on the swelling of raw I in org. liquids of various types shows that an initial gain in wt. resulting from absorption is followed by a continuous loss of wt. resulting from diffusion of I from the swollen masses. This diffusion continued, even in relatively poor swelling agents, until all but the protein had dispersed (several yrs. were necessary). This is evidence against the existence of "sol" and "gel" fractions, particularly since the points at which diffusion became very slow in different solvents corresponded to far different proportions of the total I. The proportion which diffuses readily depends upon the swelling power and upon the viscosity of the liquid, and in a given liquid the proportion can be increased by various means, *e. g.*, by the addn. of small proportions of strong org. bases and acids, such as piperidine, $NHEt_2$, NaOEt and NH_3. Likewise the behavior of vulcanized I in swelling agents gives no evidence of 2 components. Contrary to general belief, vulcanized I diffuses completely in a wide variety of org. liquids (in darkness for several yrs.), *e. g.*, in BzOEt, BuOAc, MeI, $CHBr_3$, *iso*-BuCl, *o*-ClC_6H_4Me, C_6H_6, EtPrCO, valeric acid, cyclohexanone, hexyl alc., *o*-tolualdehyde, Pr_2O, di-*iso*-Bu_2NH, etc. Comparative expts. show that polystyrene (XII) (*i. e.*, autopolymerized styrene and not styrene (XIII) polymerized by heat) and certain other polymers have properties in common with I, *e. g.*, XII resembles I (quant. data are given) in that: (1) both have an "elasticity temp." below which they are hard; (2) both can be racked; (3) the longer either I or XII is kept stretched, the higher their temp., and the greater their stretching, the greater are their permanent sets; (4) both behave the same when heated and cooled alternately under a fixed stress; (5) both are stretched to rupture by very small stresses acting over long periods of time, and (6) their sols have the same viscosities under the same conditions. Unlike XII, polystyrene prepd. by heating XIII has a measurably low mol. wt., and has a

lower elasticity temp. and smaller elasticity. A product prepd. by refluxing XIII for 48 hrs. at 140° had a mol. wt. of 1920, and one from heating XIII in a closed vessel for 24 hrs. at 180° had a mol. wt. of 2180. Both became soft at 40° and easily stretched at 47°, but with a poor retraction. XII can be made elastic at room temp. by introducing a swelling agent, and recovery after deformation of such swollen XII is more nearly complete than that of XII made elastic by heat, *e. g.*, XII contg. 50% Et oleate showed no set after stretching 1300%. XII prepd. from soln. is extremely elastic and resembles raw rubber, but it gradually loses its elasticity as the solvent evaps., until it becomes friable. A non-volatile solvent (*e. g.*, tricresyl phosphate or *iso*-Am phthalate) renders XII permanently elastic. Neither XII nor polyvinyl acetate (XIV) is in the form of emulsions or suspensions during its prepn., so the peculiar state of globules in latex is not essential to the peculiar properties of I. Neither is the 2-phase (sol and gel) theory the answer, for XII and XIV are highly heterogeneous, as was shown by fractional pptn. and fractional diffusion. A synthetic methyl rubber, prepd. by thermopolymerization of dimethylbutadiene, was sepd. into fractions of different viscosities in C_6H_6. Natural rubber is probably also very heterogeneous, *i. e.*, it is a mixt. of a series of polymers of a wide range of degrees of polymerization; this agrees with its behavior in swelling agents. All fractions disperse ultimately, and though the protein may retard the diffusion, the slowness is due primarily to the high degree of polymerization. This dependence of the rate of diffusion upon the degree of polymerization was also found with vulcanized oils, with diffused I, *i. e.*, I sol (XV) when vulcanized, and with polymethyl acrylate (XVI). The latter, prepd. by heating Me acrylate with 0.1% Bz_2O_2 for 0.5 hr. on a water bath, had a mol. wt. too high to depress the f. p. of C_6H_6, had a higher degree of swelling than any polymer studied (88.8 times its wt. of MeOAc), yet did not disperse in good swelling agents. Direct exptl. evidence of the heterogeneity of raw I was obtained by fractional diffusion, which yielded sols of widely differing viscosities. XV was sepd. by fractional pptn. into fractions of different properties, and, contrary to Feuchter, Hauser and others, it is very heterogeneous. XV resembles I in that its behavior on mastication is similar, and in that it can be vulcanized (better results are obtained by adding a fatty acid), can be racked, and gives an x-ray diffraction diagram when stretched. Fractional diffusion of I yielded a 1st fraction of 5%, which was an elastic solid, and no evidence was obtained that there is a liquid phase in I. Not only is there a rough parallelism between the av. degree of polymerization and the viscosity of a polymer, but for the polymeric products prepd. by a given method from a given monomer there probably is a definite degree of polymerization where the elasticity is greatest. Below this, ready deformation is accompanied by poor recovery, and above it the product is tough or brittle. The term "*elastic yield value*" is suggested as a means of identifying imperfectly elastic colloids, such as I, XII and XIV, and distinguishing them quantitatively from the more nearly perfect elastic colloid, vulcanized rubber. This behavior is complicated at times by an accompanying change from elastic to irreversible deformation, *i. e.*, plastic flow. Furthermore, a permanent set may not result from plastic flow, but from the fact that the elastic yield value is too high at room temp. The retraction which follows heating rubber under load is probably likewise due to a reduction in the elastic yield value. Swelling agents reduce the elastic yield value of XII, XIV and hydrophilic colloids like silk fibroin and wool keratin. The ultimate explanation of elasticity in org. colloids is not yet in sight. A helical, elastic mol. (cf. Fikentscher and Mark, *C. A.* **24**, 3395) is not an explanation, for widely different mols., *e. g.*, XII, XIV, XVI, sulfurized fatty oils and proteins, are elastic, and inelastic substances are rendered elastic by swelling agents and by heating. Neither does x-ray data so far obtained offer an explanation, and evidence indicates that a pattern means that the substance is becoming inelastic. The concept of an optimal degree of polymerization for max. elasticity is fundamental in explaining vulcanization, for the progressive changes when rubber and S are heated probably represent increasing degrees of polymerization. Similarly, when dianisidine and crotonaldehyde (2 mols.) are mixed, the initial product is a thin liquid; on standing at room temp. this becomes viscous, then an elastic solid, then a tough, inelastic solid, and finally a brittle solid; this series of polymerization changes is analogous to those of rubber. The vulcanization of fatty acids throws light on the nature of vulcanization of rubber in that the progressive phys. changes are the same, and both reactions are accelerated by the same org. compds., *e. g.*, dithiocarbamates and mercaptobenzothiazole. Further expts. (cf. W. and Chataway, *C. A.* **20**, 2588) show that accelerators probably act as catalysts of the polymerization. On heating fatty oils, *e. g.*, linseed (XVII), corn, perilla and China wood (XVIII) oils, with S until part had become insol. in acetone but not in Et_2O and on removing all free S, the subsequent addn. of rubber vulcanization accelerators decreased the time of heating to cause setting to an elastic solid. Accelerators were much more effective with XVIII than with XVII; this is probably related to the fact

that XVIII contains a doubly conjugated linkage system and is converted into a solid by polymerization catalysts like $SnCl_4$ and $SbCl_5$, whereas XVII is not thus polymerized. But when heated with S, XVII became polymerizable by $SnCl_4$ and $SbCl_5$, probably because of a change in the orientation of the double bonds. By analogy, the vulcanization of I involves essentially a polymerization, and accelerators act as catalysts. As with XVII, a preliminary change by S and heat is necessary. The suggested formula of I (*loc. cit.*) shows a terminal conjugated system, and it is known that such a system often makes polymerization possible. The vulcanizing action of benzoyl peroxide, a polymerization catalyst, is in accord with the view that vulcanization is essentially polymerization. The aging of vulcanized I probably involves further polymerization by atm. O, for the latter is a polymerizing agent. The fact that hydroquinone retards aging is in accord with this view, for it is an anticatalyst of polymerization, *e. g.*, of XIII (private communication). C. C. DAVIS

Temperature regulator for ovens and bombs used for studying the aging of rubber. R. FRIC AND R. THÉVENET. *Chimie & industrie* Special No., 667–9(March, 1931); cf. F., *C. A.* **22**, 4876.—A device is described which is suitable for maintaining a const. temp. in the previously described pressure oven. The principle consists in keeping the current const. by means of a resistance which is varied automatically by a small servomotor started by a contactor operated by a contacting ammeter. A. P.-C.

Mold for stamping out annular (rubber) test pieces. R. FRIC. *Chimie & industrie* Special No., 670–1(March, 1931).—A descripion of a mold which gives satisfactory results with inexperienced operators, small quantities of material, and thick sheets directly from the mixer without calandering. A. PAPINEAU-COUTURE

Further x-ray studies of gutta-percha and balata. CHARLES W. STILLWELL AND GEORGE L. CLARK. *Ind. Eng. Chem.* **23**, 706–7(1931).—New diffraction data on gutta-percha and balata from various sources confirm the conclusion of von Susich (*C. A.* **25**, 434) that these substances are interconvertible modifications of the same substance. It was further found that the diffraction pattern of balata is almost all contained in that of gutta-percha. This suggests that gutta-percha consists of a mixt. of balata and another cryst. substance, this latter substance becoming dispersed in an amorphous state when gutta-percha is converted into balata. The practical utility of the diffraction method as a means of classification is considered. WARREN W. NICHOLAS

An x-ray diffraction study of chicle. CHARLES W. STILLWELL. *Ind. Eng. Chem.* **23**, 703–6(1931).—X-ray diffraction patterns were obtained of both crude and refined chicle. These were compared with patterns from the various fractions into which chicle may be conveniently sepd. by extn. and pptn. It was found that crude chicle is a phys. mixt. of some amorphous material with at least 3 cryst. substances, *viz.*, $CaC_2O_4 \cdot H_2O$, the resin and the gutta. The latter is probably highly dispersed and amorphous in refined chicle; otherwise crude chicle has the same structure as the refined product. Chicle gutta is identical with gutta-percha and balata, its exact nature being subject to a question of interpretation of data. Stretching chicle does not produce preferred orientation of the structural units. WARREN W. NICHOLAS

Studies on the combination of organic accelerators for rubber vulcanization. I. S. MINATOYA, K. KOJIMA AND I. NAGAI. *J. Soc. Chem. Ind., Japan* **34**, Suppl. binding No. 4, 138–40(1931).—In expts. on the m. ps. of mixts. of varying proportions of org. accelerators, m. p. curves were obtained which resembled metallographic eutectic curves. Thus mixts. of mercaptobenzothiazole (I) and diphenylguanidine (II) gave 2 eutectic mixts. (III and IV) and a mol. compd. (V). The eutectic mixts. were at 130° with approx. 8% I, and at 144° with approx. 57% I. The mol. compd. was at a mol. ratio of 1:1. The tendency of the mixts.: smoked sheet 100, S 5, ZnO 100, I, II, III, IV or V, resp., 1, to scorch was then studied by heating the mixts. at 70° and at 100°, resp., for 150 min. and measuring their condition each 10 min. by the turbidity method of Vogt (cf. *C. A.* **16**, 2620). At 70° no mixt. scorched, but at 100° all scorched successively, *viz.*, after 15 min. with V, nearly as soon with IV, soon after this with III and after 70 min. with I and with II. All combinations were therefore more active than the individual accelerators. Vulcanization tests of the base mixt.: smoked sheet 100, S 5, ZnO 10, accelerator 1, with the 5 accelerators, with cures for different times at 20 and at 45 lb. per sq. in. steam pressure, showed that V was by far the most powerful accelerator, IV and III were much less active and I and II still less active, *i. e.*, the accelerating actions during vulcanization were in the same order as in the scorching tests. The so-called "plateau effect" was less marked with III, IV and V than with I and II. C. C. DAVIS

Note on atmospheric cracks in elongated rubber. A. VAN ROSSEM AND H. W. TALEN. *Proc. Acad. Sci. Amsterdam* **34**, 450–3(1931).—A preliminary note. Wedge-shaped samples (thickness 1–8 mm.) of vulcanizates were exposed under tension to direct sunlight and air, so that the % elongation varied inversely with the thickness. In this

way it was possible to study with 1 sample the influence of the elongation on the tendency to crack. It was found, in agreement with the expts. of Williams (*C. A.* **20**, 2093), that the largest cracks appeared at 10–20% elongation, while at higher elongations the cracks were smaller but more numerous. The shaded sides of the samples also became cracked. On repeating the expts. in darkness (at night), similar cracks appeared after about the same length of time; hence, neither ultra-violet nor visible light caused the cracking. The prevalent term "suncracking" should therefore be discarded in favor of "atm. cracking." No final explanation of the cause of cracking under elongation is offered, though it is most probable that cracking is caused by traces of O_3. This is supported by the fact that cracking appeared soonest in stormy weather. The formation of cracks by O_3 resembles closely the cracking of alloys under tension when attacked chemically (cf. Sachs, *Z. Ver. Deut. Ing.* **71**, 1511(1927)). Cracking occurred in both raw and vulcanized rubber when stretched, but when a calender effect was present there was no cracking. Though O_3 may be the cause of cracking, it does not effect this by forming an inelastic oxidized film, as suggested by Kearsley (Kautschuk **6**, 244(1930); *C. A.* **25**, 232), because no cracking occurred when unstretched vulcanizates were exposed to O_3 and to air and were afterward elongated. C. C. DAVIS

Contribution to the chemistry of latex. I. Measurements of the surface tension of fresh latex and their relation to the non-crepe components. P. SCHOLZ. *Kautschuk* **7**, 42(1931); cf. S. and Hauser, *C. A.* **22**, 331, 511.—The method was the same as in the previous expts., and the latex was less than 4 hrs. old. The measurements, which are tabulated, give for latexes from different trees the total solids, the yields of crepe, the difference between these and the surface tension of the latex. The data show that the greater the proportion of solids which do not appear in the crepe (the difference between the wt. of total solids and the wt. of crepe), the lower is the surface tension of the latex. This confirms the conclusion of the earlier expts., that the substances which control the surface tension of latex, and make it so much lower than that of water, remain behind in the serum when the latex is coagulated. **II. Two new and simple methods for determining the dry content and the crepe content in the latex of Hevea brasiliensis, with a precise and rapid method developed from these for determining the crepe content in a unit volume.** PAUL SCHOLZ AND KARL KLOTZ. *Ibid* 66–8.—Products of more recent importance, *e. g.*, crepe soles and Revertex, make highly desirable a more accurate method for detg. the yield of crepe from a latex. *Detn. of total solids.*—Spread out in a shallow Ni dish (10-cc. diam.) approx. 2 g. of latex (within 1 mg. by dropping from a glass tube weighed before and after), evap. slowly with gentle heat (a skim is broken by an air jet and later by a weighed rod) until all water is gone, as evidenced by the disappearance of any white opaque spots, roll up the film immediately to avoid absorption of water, and weigh. This method has a precision of $\pm 0.1\%$ and can be carried out in 6–7 min. *Detn. of yield of crepe. By wt.*—To 25 g. of latex (the wt. precise to 1 mg. as before) in a Petri dish add dropwise 10–20 cc. of 10% H_2SO_4, let stand 10 min., remove the coagulum without pressing, wash for 2 hrs. in running water at 50° (until there is no acid reaction of the coagulum pressed on litmus paper), press between cloth, and dry at 70–85° until no white or opaque spots remain and the product is uniformly clear amber. The detn. is not reliable if there are black spots or if the product is sticky. *By vol.*—The same method is used, except that 25 cc. (from a pipet, which must be rinsed) is coagulated. This method is precise to $\pm 0.1\%$, and was checked against practical yields of 200 lb. of crepe. An alternative simple method is to dil. 10 g. or 10 cc. of latex 2–3 fold, add 10% AcOH, heat in a Petri dish on the water bath until coagulation is complete, rinse the coagulum, squeeze thin, boil in water 0.25–0.5 hr., press and dry. Comparative tests of 1000 detns. over 2 yr. showed that the vol. yield of crepe was approx. 0.9 that of the total solids, and this was found to be true of data of de Vries (cf. *Estate Rubber*) and of de Haas (*Ann. Bot.* 3rd Suppl. **1910**, 443) when interpreted in this way. By assuming a d. of 0.98 for latex, this gives the relation: $C_w = 0.92\ (TS)$, or in general: $Cw = [0.9(TS)]/d$, where C_w is the % yield of crepe (by wt.), (TS) is the % total solids, and d is the d. of the latex. In this way a detn. of 1 value will give reliable data on both yields, so that a detn. of total solids requiring less than 10 min. will replace the tedious methods used heretofore for detg. directly the yield of crepe. C. C. DAVIS

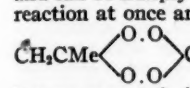
Investigations of the manganese and iron contents of different types of crude rubber and rubber fillers, and their relation to the development of stickiness and to the deterioration of rubber. F. KIRCHHOF. *Kautschuk* **7**, 26–33(1931).—Examn. of various types of plantation and wild rubbers showed that small percentages of Mn are normally present in all types of crude rubber. Plantation *Hevea* rubbers after washing contained normally only a few hundredths or at the most a few tenths of a mg. of Mn per 100 g. of rubber, whereas wild rubbers contained 0.5–2.0 mg. of Mn

per 100 g. Crude *Tjipetir* gutta-percha had a relatively high Mn content. Compared with rubbers in a sound condition, rubbers of the same types in a tacky or sticky condition contained several times as much Mn, and were also abnormally high in Fe. These relatively high Mn and Fe contents do not depend upon relatively high ash contents, for there was no relation between the % Mn and % ash, and on washing rubbers the ash and the Mn contents were not reduced in the same proportion. This suggests that the Mn is combined at least in part with insol. org. non-rubber components (probably proteins), and in sticky rubbers it is combined in part with C_6H_6-sol. decompn. products (perhaps oxidation products of the rubber). In any case the abnormally low viscosities (in C_6H_6) of sticky rubbers were proportional to the Mn contents of the dissolved part. No traces of Mn were present in the acetone-sol. part of sticky rubbers. Mn contents of about 7 mg. per 100 g. of rubber, accompanied by 100 or so times as much Fe, bring about stickiness in rubber, which may be termed a "liquefaction." The latter is regarded as an oxidation-depolymerization, in which the Mn compds., in conjunction with Fe oxides and probably also with org. catalysts (cf. Bamber and Spence, *Kolloid-Z.* **4**, 71(1909)), act as oxidation-reduction catalysts. Following this "liquefaction" there is a drying (resinification) similar to that of oil varnishes, which forms hard, lacquer-like coatings, while the decompd. hydrocarbon chains are condensed through O bridges to resinous complexes. The proportion of dark-colored, C_6H_6-insol. non-rubber part contg. high Fe and Mn is a measure of the tendency of a rubber to become sticky and for its vulcanizates to age poorly. Mn in quantities from a few hundredths to a few tenths of 1% was also found in all mineral fillers from natural sources, including whiting, barytes and Fe oxides. Such quantities of Mn may result in a rapid deterioration of vulcanizates compounded with them. With Mn present in vulcanizates, the initial change on aging is a depolymerization brought about by the Mn catalyst, and this change is evidenced by a large increase in the % acetone ext. Examn. of vulcanized products indicates that Mn contents around 0.05% or more (based on the rubber content of the vulcanizate) are to be regarded as dangerous to good aging, particularly when rather large proportions of Fe oxides are also present. Much more experimentation is necessary before the complicated role played by Mn can be explained in detail. The smoked sheets and the pale crepe also contained 2 mg. and 1.5 mg., resp., of Cu per g. of ash (0.5–0.75 kg. of rubber), whereas in the wild rubbers and in the sticky rubbers there were not even traces in the ash. This Cu may be picked up by bronze washing rolls on the plantations. Not every kind of tackiness or stickiness in rubber is to be attributed to Mn, Fe or Cu, for heat alone brings about a kind of stickiness, but the latter does not change the viscosity or vulcanizing properties of the rubber. For *detg. Mn*, the colorimetric method involving oxidation in HNO_3 to $KMnO_4$ by PbO_2 is applicable when the ash contains considerable Fe but little or no C. But the ash of many plantation rubbers retains C and this disturbs the $KMnO_4$ reaction. It is best to treat 0.2 g. of ash with 20–5 cc. of 2 *N* H_2SO_4, heat to boiling, filter, add to the filtrate 5 cc. of 2 *N* HNO_3, about 0.5 g. of pure PbO_2 and a few drops of aq. $AgNO_3$ (to remove chlorides), boil 5–10 min., let stand in darkness, remove a part of the clear supernatant liquid and compare with 0.005 *N* $KMnO_4$ in a Dubosc colorimeter. For very pale solns., the standard soln. should be 0.001 *N* $KMnO_4$. A C-free ash can be heated directly with 2 *N* HNO_3 and PbO_2, but in this case 2 or 3 treatments are necessary before the liquid becomes colorless on further treatment. The method used by Bruni and Pellizola in similar expts. (cf. *C. A.* **15**, 3567) with oxidation by $K_2S_2O_8$ gives a $KMnO_4$ soln. which is not so stable nor so bluish as that from treatment with PbO_2, and furthermore when the PbO_2 ppts. it adsorbs and thus removes traces of AgCl so that the soln. clears rapidly. C. C. DAVIS

Investigations of the manganese and iron contents of different types of crude rubber and rubber fillers, and their relation to the development of stickiness and to the deterioration of rubber. FRITZ FRANK. *Kautschuk* **7**, 75(1931).—Comments on an article by Kirchhof (cf. preceding abstr.). C. C. DAVIS

Rubber. XII. Levulinic acid peroxide from rubber. RUDOLF PUMMERER, GEORG EBERMAYER AND KARL GERLACH. *Ber.* **64B**, 804–9(1931); cf. *C. A.* **25**, 1410.—Harries' levulinaldehyde diperoxide (I) (the authors prefer to call it *levulinic acid peroxide*) is formed not only by "over-ozonization" of rubber ozonide but also when the ozonide solns. are allowed to stand a long time, *e. g.*, in the ice box, in closed vessels. The ppt., which is often only very slight directly after the ozonization, increases considerably in the course of 8–14 days, and may amount to 15–20% of the C skeleton of the rubber; it is therefore a decompn. product of the rubber ozonide, formed in an indifferent medium, possibly by traces of moisture. The m. p. of the crude product varies from 173° to 190°, and may be raised by crystn. from H_2O to 196°. Analysis and mol. wt. detns. (272.5 in boiling alc., 256–262.2 in dioxane) agree with the formula

$(C_5H_8O_4)_2$. Purification by pptn. from NaOH with acids does not raise the m. p. nor change the compn., but the elongated rectangular plates now show exceedingly characteristic double wedge-shaped domes. The $TiCl_3$ oxidation value in hot H_2O is 1.9 atoms of active O per mol. $(C_5H_8O_4)_2$; in cold aq. alc. after 3 hrs. or in aq. alc. or aq. Me_2CO after short heating it is 1.8 atoms. H. ascribed its soly. in alkalies to the acid character of the aldehyde H. **I**, however, dissolves even in cold $NaHCO_3$, and can be sharply titrated (equiv. wt. 132). It reacts strongly acid and gives the CHI_3 reaction at once and very strongly. The levulinic acid peroxide structure, HO_2CCH_2-



$CMeCH_2CH_2CO_2H$, is suggested for **I**. The peroxide nature of the ketone groups is inferred from the sluggishness of **I** toward $2,4\text{-}(O_2N)_2C_6H_3NHNH_2$, which with levulinic acid in 50% AcOH immediately gives the characteristic, very difficultly sol., orange-yellow hydrazone, m. 203°. Attempts to synthesize the peroxide from the aldehyde or acid with O_3 or H_2O_2 and HCl have so far been unsuccessful, however. Treated in faintly alk. soln. with Al-Hg until the Ti-H_2SO_4 reaction is neg., **I** yields more than 90% of levulinic acid. $TiCl_3$ in concd. HCl reacts with **I** very slowly (weeks are required for disappearance of the peroxide reaction), and the result is not reduction but cleavage and rearrangement (probably brought about by the acid); 1 g. **I** yields 0.42 g. levulinic acid (48% of the C skeleton), 0.33 g. $(CH_2CO_2H)_2$ (29.5%) and 0.28 g. HCO_2H (16.2%). Baeyer and Villiger observed the rearrangement of ketone peroxides into acid esters, and possibly a peroxide of the type $MeC(:O_2)CH_2$-CH_2CO_2H would rearrange into $MeO_2CCH_2CH_2CO_2H$; as a matter of fact, when **I** is boiled in H_2O in a flask connected to a condenser, MeOH can be detected in the distillate in small amt., but apparently most of it is oxidized to HCO_2H by the peroxide O of the other half of the mol. This, however, does not account for all the HCO_2H found (1.6 mols. per mol. **I**), so that the decompn. of half of the mol. is probably more complicated than the rearrangement above. In cold alc. neutral soln., H and Pt do not react with **I** in the cold, and on heating again give levulinic and succinic acids. **XIII. Ozone degradation of rubber.** *Ibid* 809–25.—Harries and his pupils found only levulinic aldehyde and acid among the cleavage products in the O_3 degradation of rubber and concluded that, contrary to the Weber open-chain formulation, rubber consists of $—CH_2CMe:CHCH_2—$ residues recurring in a ring form. They found HCHO or HCO_2H, to be sure, among the cleavage products, but this is not specific, since HCHO can be obtained by the ozonization even of hexane. In spite of diligent search on large quantities of rubber they found no Me_2CO, glyoxal or AcOH, which would be expected from the ends of the chain if rubber had the open-chain structure. This view that no end members can be detected has, however, not been sufficiently well established experimentally. Based on the C skeleton of the rubber used, their % yields of cleavage products recovered were: levulinaldehyde as pyridazine 1.24, pure levulinaldehyde 10.90, levulinic acid 44.10, HCO_2H 0.56, succinic acid 0.17, ozonization residue 9.1, leaving 43.93% unaccounted for. Since, at the present day, very long chain formulas play an important role, the need of improving the yields in the cleavage is quite evident. Moreover, a prerequisite for the validity of conclusions as to the av. length of the chain drawn from the cleavage products is that the rubber should contain no structurally-foreign impurities. As quite pure rubber and a no. of rubber fractions are now available, it is possible to estimate more or less which cleavage product is derived from an impurity and which is not. The authors at first used the Harries method of decompg. the ozonides with boiling H_2O and distg. the volatile products with steam, but as secondary reactions, such as oxidative cleavage of the levulinic acid, and rearrangements, such as that of the levulinic acid peroxide, occur, they gradually adopted milder and milder conditions. Steam was passed in for the shortest possible time to decomp. the ozonide, and the volatile products were distd. off with steam *in vacuo*. The steam decompn. has advantages in testing for definite cleavage products such as Me_2Co. In order, however, to avoid the formation of abnormal cleavage products, it is better not to raise the temp. at all, as by boiling in H_2O or even glacial AcOH. Consequently, after the ozonization (with 3–4% O_3 in $CHCl_3$), chiefly reductive cleavage was effected, either catalytically with Pt sponge and H, or with nascent H. After removing the $CHCl_3$ in a high vacuum, neutral cleavage was effected with Ca shavings and oxalic acid or with Al-Hg. The rubber ozonide is at first sol. in $CHCl_3$, but on long standing deposits considerable quantities of cryst. levulinic acid peroxide (see preceding abstr.), in which form a part of the levulinic acid can be weighed; when the $CHCl_3$ is filtered off, the ozonide remains Et_2O-sol. and can easily be reduced, whereas when isolated immediately after the ozonization it is difficultly sol. in Et_2O and must be stirred very vigorously for the reduction. By such improvements in the method,

the authors have come much closer to the goal of a really quant. ozonide cleavage of rubber, but have not yet quite reached it. By conservative calcn., the total yield of cleavage products, based on the C skeleton of the rubber used, is 95%. The authors did not limit themselves to designating a given fraction as levulinic acid or aldehyde on the basis of its b. p., but analyzed the cleavage solns. by titration and quant. pptn. with reagents. The yield of levulinic acid derivs. is around 90%. New cleavage products detected were AcOH (min. thus far, 2%), traces of Me_2Co (probably from an impurity) and a substance fermentable by dry yeast (probably $AcCO_2H$). About 1–2% each (min., 0.9%) of CO_2 and HCO_2H were found, as also varying quantities of succinic acid, probably resulting from rearrangement of the levulinic acid peroxide (see preceding abstr.). Data for a rubber gel purified with alkali, a crepe sol, 3 crepe sol fractions and a total rubber are given. The origin of the AcOH and $AcCO_2H$(?) still remains to be detd.; it cannot be ascribed to any definite end member of a chain, but neither can it be asserted that there are no such end members. **XIV. The behavior of rubber toward chlorine iodide and toward dithiocyanogen.** RUDOLF PUMMERER AND HERMANN STARK. *Ibid* 825–30.—The study of the carotenoids has shown that a large excess of ClI must be used to obtain correct results on the no. of double bonds in compds. with conjugated systems; thus, isoprene with 150% of the calcd. amt. of ClI showed only 1.77 and 1.80 double bonds after 1 day and 1 week, resp., and only with 200% and more ClI was the correct value of 2 obtained. This made it necessary to repeat the detns. which had been made on rubber (*C. A.* **24**, 1103). The new investigation showed that 110–20% ClI (*i. e.*, 10–20% more than 1 mol. ClI per C_5H_8) gives correct results, and at the same time very little or no acid appears in the titration. On the other hand, a larger excess of ClI gives materially higher I nos. (*e. g.*, 147% of the calcd. with 200% ClI), apparently because of substitution. The earlier work had, by chance, been done within the most favorable range of ClI excess, so that the results then obtained for rubber sol require no material correction. For rubber sol from latex purified with alkali and for 6 fractions from crepe, extd. cold with Me_2CO and fractionally dissolved cold with Et_2O, were obtained values ranging from 99.6 to 100.3% of the calcd. Rubber gel gave 99.1–99.3% of the calcd. values. As before, the rubber was dissolved in $CHCl_3$ in N, but the ClI was used in CCl_4, in which it is more stable and forms less acid than in $CHCl_3$. The limits of error are ±0.3%. The results with isoprene indicate that to detect an end isoprene group as a conjugated system in rubber about 200% ClI would be required, but the C skeleton of rubber would not stand such an excess without substitution, so that ClI cannot be used for the detection of an isoprene group. To det. whether the halogen acid obtained with a large excess of ClI is due to substitution or to regeneration of the double bond by elimination of HX, vinyl bromide was titrated with ClI. It reacts considerably more slowly than an ordinary olefin, but with 180% ClI it was completely satd. in 50 hrs. CHCl:CHCl, on the other hand, reacts practically not at all. Limonene behaves like rubber; a 15–20% excess of ClI gives 99% of the calcd. value for 2 double bonds, a 50% excess 104% of the calcd. value. The use of $(SCN)_2$ instead of ClI has no advantages, partly because the soln. becomes gelatinous, making the taking of samples and working up of the thiocyanate at definite time intervals very difficult. There is only a relatively short period during which the consumption of $(SCN)_2$ is const. and before the excess of $(SCN)_2$ begins to decomp. Nevertheless, in a series of detns. at 5–10-min. intervals during this period of constancy, values were obtained corresponding to the addn. of 1 mol. $(SCN)_2$ per C_5H_8 group (96–100% of the calcd. values, both for sol and gel rubber). The period of constancy can be obtained only at 0° and for 10–25 min.; in dry CCl_4 (under CO_2) it is reached in 30–60 min., in $CHCl_3$ in 1-2 days. The isolation of the analytically pure thiocyanate cannot always be effected, even when the reaction has been interrupted at the right moment; the N and S contents are usually close to the calcd. values, but O is easily taken up during the working up of the product. Excess of polymerized $(SCN)_2$ can be removed by extn. with hot Me_2CO. C. A. R.

Rubber micelles or macromolecules? H. LOEWEN. *Kautschuk* **7**, 12–4(1931).—Comments on the views of Staudinger as expressed particularly in a recent work (cf. S. and Joseph, *C. A.* **25**, 2591). The arguments in favor of the existence of macromols. are not convincing, and the view is upheld, in common with Meyer (cf. *C. A.* **23**, 1623), that in its solns. rubber is in the form of micelles. C. C. DAVIS

Rubber micelles or macromolecules? H. STAUDINGER. *Kautschuk* **7**, 47–8 (1931).—A reply to Loewen (cf. preceding abstr.). The expts. of Herzog on cellulose (cf. *C. A.* **19**, 3373) are at variance with more recent expts. on cellulose by S. and Freudenberger (*C. A.* **25**, 280) and S. and Schweitzer (*Ber.* **63**, 3132(1930)) and lose their significance as a support for the Meyer micellar theory of rubber. The extensive investigations of S. and his collaborators on the constitution of synthetic high-mol. compds.

are of much more importance in explaining the constitution of rubber, particularly those dealing with the relation between mol. wt. and viscosity. C. C. DAVIS

An example of scientific and economical preparation of smoked plantation rubber. N. H. v. HARPEN. *Kautschuk* **7**, 108–10(1931).—A realization that the thickness of smoked sheet as now marketed is wholly empirical, and may not be near the ideal for economy and keeping quality, led to expts. on the drying problem and a study of the economy of different thicknesses of sheet. Sheets 1.25, 1.70, 1.80, 2.20, 3.00, 3.94 and 4.47 mm. thick required 24, 48, 52, 76, 140, 235 and 340 hrs., resp., at 45° to dry under conditions otherwise const.; from these results through graphical representation the relation: $t = 15.85\ d^2$, was derived, where t is the time (hrs.) and d is the thickness (mm.). This shows the economic necessity, barring other disadvantages, of prepg. smoked sheet as thin as practicable. Based on these results, calcns. show the savings possible in plantation production by the prepn. of thinner sheet, taking into account the time of drying, capacity, fuel consumption, etc. Aside from increased economy of production, the proportion of rubber of higher quality is increased, very thin smoked sheet can be washed more easily and deterioration by microörganisms is lessened. Comparative tests of the vulcanizing properties and quality of the vulcanizates showed that very thin smoked sheet is fully as good as the present market type. C. C. D.

Sealing materials for tire inner tubes. J. B. MEYER. *Kunststoffe* **21**, 103–4 (1931).—A patent review. J. M. PERRY

The impregnation [of textile fabrics by rubber]. E. A. HAUSER WITH M. HÜNEMÖRDER. *Kautschuk* **7**, 89–94(1931).—Substantially the same as *C. A.* **25**, 3197. C. C. DAVIS

Value of softeners in tread stock. M. J. DEFRANCE AND W. J. KRANTZ. *Ind. Eng. Chem.* **23**, 824–7(1931).—To the base mixt.: rubber 100, S 3, mercaptobenzothiazole 1.25, ZnO 5, gas black 40, stearic acid (I) 4, were added different proportions of pine tar (II) and "mineral rubber" (III), and to the same base mixt. without I were added different proportions of I. The plasticities of the mixts. contg. II and III were detd., and the mixts. were examd. for their tensile properties and for their resistances to abrasion both in service on the road and on 4 lab. abrasion machines. The results are given in graphical form. Both II and III were detrimental to quality and should be kept at a min. The best proportion of I was 4% of the rubber. The lab. abrasion tests were indicative of road wear, but were not in agreement. C. C. DAVIS

The examination of factice. GRANDEL & CO. *Kautschuk* **7**, 48–54(1931).—No methods of analysis of brown and white factice have been published heretofore. A proximate analysis should include (1) color, (2) odor, (3) qual. unsaponifiable, (4) m. p. or behavior on heating, (5) d., (6) acidity or alky., (7) moisture and (8) impurities; a closer exman. should include: (9) total S, (10) Cl, (11) acetone ext., (12) free S in the acetone ext., (13) total S in the acetone ext., (14) combined S in the acetone-insol. part, (15) m. p. of the acetone-insol. part, (16) quant. unsaponifiable and (17) ash. (1) and (2) depend upon the type of factice, and must be judged by the circumstances. (3). Reflux 80–100 mg. of finely ground factice with alc. KOH (1 g. in 5 cc. abs. EtOH) for 0.25 hr., filter and dil. the filtrate with hot water (5 cc.). A turbidity indicates unsaponifiable. Three % can be detected thus. (4). Heat the factice (finely ground) in a test tube in a paraffin-oil bath at a rate of 2–3° per min., so that the bath runs about 10° higher than the factice. (5). When finely ground, det. the d. by boiling the factice in satd. aq. NaCl (or KBr if the d. is higher), dil. the soln. until the factice just floats, and det. the d. of the soln. (6). Brown factice should be neutral, white factice, neutral or alk. Ext. by agitation with cold water (1:20), filter and test the filtrate with Congo red for acidity, and with phenolphthalein for alky. (7). Dry the finely ground factice (5 g.) at 105°. The results with white factice may be erroneous because of gaseous losses. (8). Agitate the finely ground factice (1 g.) with CCl_4 (10 cc.), and exam. by transmitted light the swollen, transparent product for mech. impurities. (9). Heat cautiously an intimate mixt. of the factice (0.5–0.7 g.), Na_2CO_3 (7.5 g.) and KNO_3 (7.5 g.) in a Ni crucible until a clear liquid is obtained (after about 1 hr.), cool, ext. with water (150 cc.) on a water bath, add cautiously to the soln. HCl (d. 1.19) until strongly acid, heat until most of the nitrous vapors are expelled, filter, bring to boiling, and ppt. $BaSO_4$ in the ordinary way. (10). Fuse, as in (9), a mixt. of factice (0.5–1.0 g.), Na_2CO_3 and KNO_3, ext., acidify with HNO_3, filter and ppt. with $AgNO_3$. The Cl may also be detd. volumetrically by the Volhard method, from the HNO_3 soln. described above. (11). Ext. the finely ground factice (5 g.) in a Soxhlet app. and dry at 90–100°. (12). To the weighed dried acetone ext. add a mixt. of C_6H_6 and acetone (25 cc. of 1:1) satd. with S, close the flask, rotate several min., let stand for 2 hrs. with periodical agitation, decant, wash the S residue twice with 2 cc. of acetone, dry at 90° and weigh the free S. The acetone must be anhyd. In de-

veloping this method involving a soln. satd. with S, preliminary expts. were carried out to det. the *soly. of S in various solvents*. The following data show the no. of g. of S in 1 cc. of solvent at room temp.: AcMe 0.0006, Et_2O 0.0016, 75% EtOH 0.0001, AcOAm 0.0020, C_6H_6 0.0160, $CHCl_3$ 0.0135, petr. ether 0.0016, CCl_4 0.0111, EtOH-Et_2O (1:1) 0.0009, C_6H_6-AcMe (1:1) 0.0028, C_6H_6-petr. ether (1:1) 0.0066. (13). Dissolve the acetone ext. in a min. of C_6H_6, add to a Na_2CO_3-KNO_3 mixt. (see (9)) (15 g.) in a Ni crucible, evap. the C_6H_6, cover with more Na_2CO_3-KNO_3 mixt. (10 g.), and follow the same procedure as for (9). (14). This is important for factices contg. mineral oil. Follow the same procedure as with (9), using the dried residual part of the factice which remains after acetone extn. (15). Follow the same procedure as in (4). This gives an indication of the quality of oil used in making the factice. (16). Reflux the finely ground factice (2 g.) in 2 *N* alc. KOH (15 cc.) for 0.5 hr., add water (15 cc.) (if not a clear soln., boil the soln.), put in a separator (rinsing with 25 cc. of 50% EtOH), ext. 3 times with petr. ether (b. 30–50°, 50 cc. each time), wash the petr. ether ext. with 50% EtOH (25 cc. contg. a little KOH), ext. 2–3 times with 50% EtOH (25 cc. each time), evap. the petr. ether residue in a weighed flask, and dry at 90–100°. If the factice is not completely ash-free, part of the ash remains in the petr. ether soln. and is weighed. Either filter through a dense filter immediately after the sapon., or filter the petr.-ether soln. of the unsaponifiable. The 2nd alternative is preferable because of the greater ease of filtration. If soap remains in the unsaponifiable, the soap can be detd. by addn. of a known quantity of 0.1 *N* HCl and back titration of the unconsumed acid with 0.1 *N* KOH. Rapeseed oil contains 0.4–1.5% unsaponifiable, so that a small proportion of unsaponifiable in factice may indicate that the factice was made from this oil. (17). A qual. analysis of the ash may be advisable to ascertain whether any components deleterious to rubber are present. C. C. DAVIS

Accelerators of vulcanization. F. JACOBS. *Caoutchouc & gutta-percha* **28**, 15562–5 (1931); cf. *Caoutchouc & gutta-percha* **28**, 15485; cf. *C. A.* **25**, 3872.—The properties and behavior as an accelerator of mercaptobenzothiazole disulfide (the com. "Altax") are described. C. C. DAVIS

Some considerations of latex processes. D. F. TWISS. *Trans. Inst. Rubber Industry* **6**, 419–30(1931).—A crit. review and discussion, with particular reference to exptl. developments at the Dunlop Rubber Co. (Birmingham). Numerous patents are cited. Since centrifuging removes all kinds of non-rubber serum components, it is desirable with Utermark latex to add more protective colloid, such as casein, before making acid positively charged latex. The p_H value at which the globules of ordinary latex pass through the neutral stage (isoelec. point) can be estd. by observing microscopically the electrophoretic movements in small samples with various p_H values. The following data give the p_H at the isoelec. point, and show that the isoelec. point varies with the condition of the latex (cf. Fullerton, *C. A.* **25**, 3514) and the nature of the protective colloid: ordinary preserved latex, approx. 4.2 (difficult detn. on account of coagulation); blown dialyzed latex, 4.2; putrefied dialyzed latex, gradual decrease to 3.7–3.6; Utermark latex, 4.3–4.2; Utermark skim, 4.0; ordinary preserved latex neutralized with HCHO, 4.1; Utermark latex preserved on plantation with saponin and HCHO, 3.3. The isoelec. point of the globule also depends upon the nature of the predominant colloid. With protective colloids of the complex sulfonate type, the inversion which occurs normally at p_H 4.5 does not occur even at p_H 2. The following data give the colloid added, the no. of g. of colloid per 100 cc. of 33% rubber latex or 33% clay dispersion, the p_H inversion point of latex + addnl. colloid and the inversion point of a clay suspension with the same addnl. colloid, resp.: none, 0, 4.2–4.1, none above 2; casein, 2, 4.4, 4.6; gelatin, 2, 4.8–4.7, 4.7; hemoglobin, 1, 4.9, 6.7; saponin, 2, 3.9–3.8, none above 2; licorice, 2, 3.5–3.4, none above 2; dextrin, 2, 3.7, none above 2; gum tragacanth, 2, none above 2, none above 2; Na methylenenaphthalenesulfonate, 2, none above 2, none above 2. Though this points to the incorrectness of the idea of a substantial protein sheath around the globule, it also indicates that the non-rubber colloid present in or adsorbed on the rubber globule influences greatly the elec. behavior of the globule by governing its elec. charge and the ease of inversion. The colloid present naturally has elec. properties comparable with those of casein. C. C. D.

Latex concentration. RUDOLF DITMAR. *Kolloid-Z.* **55**, 365–6(1931).—Patent review. ARTHUR FLEISCHER

Concentrated latex and its industrial uses. Some applications on the industrial scale. F. W. WARREN. *Trans. Inst. Rubber Industry* **6**, 431–7(1931).—An illustrated description of developments at the Chas. Macintosh Co. (Manchester). The 1st satisfactory practical method for concg. latex was found to be simple evapn. near the b. p. with const. stirring and the addn. of protective colloids, such as casein and gelatin, until the rubber content was around 50%. Later, with 2% gelatin (based on the

rubber), concd. latex was prepd. by slight evapn., followed by standing until creamed. This process was subsequently abandoned in favor of the Utermark process. With heavily compounded mixts., addn. of the dispersions is followed by further evapn. by heat in a Twiss concentrator. The plant illustrated handles 500,000 lb. (dry wt.) of compounded latex per year. Developments in the transport of latex, prepn. of compounded latex, dipped balloons, gloves and tennis handles, compounded sheet, proofed fabric and electrodeposited goods are also described. C. C. DAVIS

The uses of concentrated latex. J. H. CARRINGTON. *Trans. Inst. Rubber Industry* **6**, 438–52(1931).—A crit. review and discussion, with many references, including concn. by creaming, filtration, evapn. and centrifuging, the properties of latex concentrates, control tests, compounding, general methods of manuf., *i. e.*, impregnating, spreading and doubling, spraying, dipping, electrodeposition, gelling, extruding, molding and drying, agglomeration and vulcanization. C. C. DAVIS

Manganese in raw rubber. R. O. BISHOP AND K. C. SEKAR. Rubber Research Inst. Malaya, *Quart. J.* **2**, 239–45(1931).—Analysis of ordinary plantation crepe, 2nd fraction crepe, smoked sheet, Para rubber and slab rubber showed 0.11, 0.37, 0.14, 0.17 and 0.15, resp., mg. of Mn per 100 g. of rubber; these values agree remarkably closely with the results of Bruni (cf. *C. A.* **15**, 3567). To det. the aging of raw rubber contg. different proportions of Mn added as $KMnO_4$, latex diluted to 15% rubber content was treated with different quantities of $KMnO_4$, coagulated with HCO_2H and made into sheet. The following data show the mg. of Mn per 100 g. of rubber added to the latex, the mg. of Mn per 100 g. of finished sheet and the condition of the sheet after 300 hrs. in an oven at 50–5°: 0, 0.26, no stickiness; 23.5, 3.26, slightly sticky; 35.5, 4.54, more sticky; 47.5, 5.30, still more sticky, but still only slightly so. A greater part of the Mn was removed during coagulation and washing, but the Mn remaining was sufficient to cause stickiness. When aq. $KMnO_4$ was dropped on crepe rubber, and the latter hung in air at 29–32°, the spotted parts of the crepe became sticky when the concn. of the soln. was 0.05 mg. or more per 100 cc. Rubber prepd. from latex to which $KMnO_4$ had been added vulcanized more slowly than the corresponding mixts. contg. no added $KMnO_4$. Treatment of latex or raw rubber with $KMnO_4$ is therefore inadvisable. Furthermore, $KMnO_4$ is only a weak disinfectant, particularly at low concns., and its use as a fungicidal agent is unwise. The Mn was detd. by incinerating the rubber, fusing the ash with fusion mixt., dissolving in water, pouring into concd. H_2SO_4-HNO_3 mixt., filtering, diluting and detg. the Mn in an aliquot part by the addn. of KIO_4 and comparing with known solns. in a Klett colorimeter. In a typical test case, $KMnO_4$ was added to the ash of the rubber, and an actual addn. of 0.005 g. per 100 g. of rubber analyzed 0.004 g. C. C. DAVIS

Testing results compared. I. How different laboratories check each other on various tests. W. L. STURTEVANT. *India Rubber World* **84**, No. 2, 55–7(1931).—Comparative tensile strength and elongation tests of the same vulcanized samples (different types of mixts.) by 5 different industrial labs. showed that the variations encountered depended upon differences in the style and condition of the cutting dies more than upon any other factor. Differing temp. conditions during storage and testing were also of importance, but relatively less so. **II. How different laboratories check on adhesion and flexing tests of belting and belting duck.** *Ibid* No. 4, 61–2.—Comparative adhesion and flexing tests of the same belt and comparative breaking tests of the same duck by different labs. are described, and the detailed results are recorded in tables. C. C. DAVIS

Methods for determining the physical properties of certain rubber compounds at low stresses. R. L. TEMPLIN AND R. G. STURM. *Proc. Am. Soc. Testing Materials* (preprint) **90**, 1–13(1931).—The new app. and technic which are described and illustrated make possible detns. of the phys. properties of rubber mixts. with elasticity moduli of 500–50,000 lb. per sq. in. To attain the sensitivity and precision required, special loading app. and measuring devices of wholly new character were developed. The exptl. detns. included moduli of elasticity under tension and compression in 3 directions, Poisson's ratio, permanent set, elastic hysteresis, rate of creep or time-yield, d., coeff. of thermal expansion and effects of water absorption. The data are recorded in graphs and tables, but the compns. of the rubber mixts. and their vulcanization are not described. C. C. DAVIS

Permeability of rubber to air. II. Effect of stretch, thickness, milling, compounding ingredients, kind of crude rubber and temperature of vulcanization. V. N. MORRIS. *Ind. Eng. Chem.* **23**, 837–43(1931); cf. *C. A.* **24**, 988.—The expts. are closely related to those of Daynes (cf. *Trans. Inst. Rubber Industry* **3**, 428(1928)). The vulcanizates used in the greater part of the expts. were derived from the base mixt.: smoked sheet

100, S 2.9, di-*o*-tolylguanidine 0.6, ZnO 2.9. The permeability of rubber membranes was, in an approx. way, inversely proportional to their thickness. Most of the increase in permeability which resulted from stretching was a result of the accompanying diminution in thickness. Vulcanizates prepd. from various plantation rubbers did not vary much in permeability, whereas a corresponding vulcanizate contg. "caucho ball" was somewhat less permeable. Milling on a steam-heated mill did not change the permeability, whereas milling at first on a cold mill reduced the permeability slightly. When the state of cure was the same, the temp. of vulcanization had no influence on the permeability, and therefore the recent tendency to cure inner tubes at higher temps. should not impair their capacity for retaining air. Of 17 softeners and org. diluents tested, none lowered the permeability of the vulcanizates. On the other hand, the greater the proportion of ZnO added, the lower the permeability; in general, the change in permeability by the addn. of a compounding ingredient depends upon the nature of the latter. In this connection clay, channel gas black and blanc fixe reduced the permeability most, thermal-decompn. C and whiting least. Permeability was roughly proportional to the % vol. of rubber hydrocarbon. The app. is described and illustrated.
C. C. DAVIS

Natural and synthetic rubber. VII. Fractional precipitation of natural rubber. THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL. *J. Am. Chem. Soc.* **53**, 2733–7(1931); cf. *C. A.* **24**, 3129.—Temp.-concn. diagrams are given of the systems: natural rubber–EtOH–C_6H_6, para rubber–EtOH–C_6H_6 and synthetic rubber–EtOH–C_6H_6. When a mixt. of rubber, EtOH and C_6H_6 is heated to a temp. higher than its crit. point, until it has become completely clear, and is then allowed to cool to a temp. about 1° below its crit. point, a certain quantity of gel collects at the bottom of the container, while the supernatant liquid becomes transpareet; the gel is a mixt. of rubber and nearly all of the "protein." The supernatant liquid contains rubber practically free of "protein"; it can be decanted and yields its rubber content upon cooling or by the addn. of EtOH. If a very pure hydrocarbon is desired, the procedure is repeated. A system contg. 2.0% natural rubber, 23.1% EtOH and 74.9% C_6H_6 has a crit. temp. of 43.0°; this system at 43° seps. into 2 phases; the supernatant liquid corresponds to 0.55% N-free rubber, 30.7% EtOH and 68.75% C_6H_6; when the system is cooled to 35° it retains less than 0.1% of dissolved rubber. C. J. W.

The output of estate sheeting batteries. E. RHODES AND R. O. BISHOP. Rubber Research Inst. Malaya, *Quart. J.* **2**, 226–38(1931).—A study of the av. practice on 200 Malayan estates, in conjunction with expts. at the Institute, showed that the sheeting batteries on the majority are inefficient, and the handling of the coagulum can be greatly improved. Excellent sheet can be produced at rates which are far greater than the practice heretofore, *e. g.*, tanks 18 in. deep and mills with rolls 24 in. wide can be made to produce sheet of standard quality, 18 in. wide, at rates up to 1400 lb. of dry sheet per hr.
C. C. DAVIS

Effect of scrap-drying temperature on the quality of reclaimed rubber. HENRY F. PALMER, GEORGE W. MILLER AND JOHN E. BROTHERS. *Ind. Eng. Chem.* **23**, 821–4 (1931).—From the fact that the higher the temp. of drying the more tacky a reclaimed rubber is, has arisen the belief that relatively high drying temps. would give products of poor phys. and aging properties. Accordingly a study was made of the influence of the drying temp. on the quality of 2 reclaimed rubbers, from whole tires and from inner tubes, resp., by the alkali process. The reclaimed tire scrap was dried at 75–85°, 225°, 250° and 275°F., the reclaimed tube scrap at 75–85°, 210°, 235° and 260°F., to moisture contents of 1.2–1.6 and 1.2–2.7%, resp. The higher the temp. of drying the higher the $CHCl_3$ ext. of the raw reclaimed rubber and the softer and tackier it was, whereas the acetone ext. was the same for the different temps. The drying temps. of 275°F. and 260°F. (the highest tested) for the reclaimed tires and tubes marked the points above which damage to the phys. quality of the uncured products became evident. A max. ultimate drying temp. of 250°F. to a min. of 3% moisture is advised for all types of reclaimed rubber, and it is recommended that much lower ultimate temps. be used and more rapid drying accomplished by higher temps. at the wet end of the drier. Cured with S alone, the vulcanizates with each reclaimed rubber were less stiff the higher the temp. of drying. When the reclaimed rubber was cured in accelerated mixts. contg. also new rubber (around 35% by wt. of reclaimed rubber), the rate of vulcanization and the tensile properties, both when new and after aging in the 70° air oven and in the O bomb, were practically the same whatever the temp. at which the reclaimed rubbers were dried.
C. C. DAVIS

Rubber problems confronting automotive engineers. R. K. LEE. *India Rubber World* **84**, No. 4, 55–7, 64(1931).—The many uses of rubber in automobiles necessitates specifications for various properties, among which are discussed the effects of temp.

and of fixed compressive loads, abrasion, mech. deflection or deformation, the proportion between movement and vol., the appearance, the effects of chem. reagents, dimensional variability and changes in phys. properties from aging. C. C. DAVIS

Difficulties in the manufacture of mechanical goods. C. R. QUARTLEY. *Trans. Inst. Rubber Industry* **6**, 453–7; *India Rubber World* **84**, No. 4, 53–4(1931).—A general discussion of molding problems, with special reference to deficient and excess vol. of rubber mixt., crippling, trapped air, surface marking and porosity. C. C. DAVIS

Scorching and other plasticity changes in rubber compounds on heating. E. O. DIETERICH AND J. M. DAVIES. *Ind. Eng. Chem., Anal. Ed.* **3**, 297–300(1931).—The method which is described utilizes the Goodrich plastometer (cf. Karrer, Davies and Dieterich, *C. A.* **24**, 1548) for ascertaining the tendency of an uncured rubber mixt. to "scorch" or begin to vulcanize. By heating the mixt. at various temps. for various times and then measuring the plasticities at room temp., the changes in the plasticity will reveal incipient vulcanization, and therefore will serve as a criterion of safe operating conditions for the rubber mixt. in practical use. Examples of the application of the method to different types of compds. are given. Stiffening and softening of uncured rubber mixts. by heating, both of which phenomena have not been previously described, were observed. In the 1st case, the mixt. gradually stiffens during heating, independently of any vulcanizing effect, and in the 2nd case the mixt. at first softens during heating before it becomes progressively stiffer. C. C. DAVIS

Isoprene and rubber. XXXIII. End groups in rubber. H. STAUDINGER. *Ber.* **64B**, 1407–8(1931); cf. *C. A.* **25**, 3872; Pummerer, Ebermayer and Gerlach, *C. A.* **25**, 4438.—The thread mols. of rubber are so long (on an av., 1000 isoprene residues) that it is quite hopeless to attempt to det. their mol. wt. by chem. reactions based on the fact that the end groups are different from the groups in between. C. A. R.

Patents

Rubber. THE ANODE RUBBER CO., LTD. Ger. 518,687, Nov. 2, 1927. See Brit. 296,138 (*C. A.* **23**, 2603).

Rubber. THE ANODE RUBBER CO., LTD. Ger. 521,749, April 18, 1926. See Brit. 269,504 (*C. A.* **22**, 1497).

Latex preservation. ALEXANDER A. NIKITIN (to Naugatuck Chemical Co.). U. S. 1,801,754, April 21. Latex is treated with a small quantity of a phenol such as PhOH and an aliphatic hydrocarbon such as kerosene, gasoline or paraffin oil.

Rubber latex dispersions. ARTHUR BIDDLE (to United Products Corp. of America). U. S. 1,801,621, April 21. An aq. dispersion suitable for use as an adhesive comprises rubber latex, an alk. earth hydroxide such as $Ca(OH)_2$ and a water-sol. "Cl substance" such as NaCl. Na_2CO_3, Na tungstate, casein, Na_3PO_4, starch, glue, S, ZnO, etc., also may be added.

Rubber dispersion suitable for waterproofing various materials. MERWYN C. TEAGUE (to General Rubber Co.). U. S. 1,802,127, April 21. An aq. dispersion of rubber is prepd. contg. a water-sol. sulfonated oil.

Apparatus for making rubber inner tire tubes by spraying latex on a rotating mandrel. CHARLES E. MAYNARD (to Fisk Rubber Co.). U. S. 1,802,120, April 21. Structural features.

Mill-roll treatment to break down rubber stock. CHARLES E. MAYNARD (to Fisk Rubber Co.). U. S. 1,802,119, April 21. Mech. features and app. are described.

"Antioxidant" for rubber. LUDWIG J. CHRISTMANN (to American Cyanamid Co.). U. S. 1,800,435, April 14. A tetra-alkyl-substituted benzidine such as tetramethylbenzidine is added to rubber compns. (suitably in the proportion of about 1%).

Coloring rubber. IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 699,659, July 28. 1930. Rubber, etc., is colored by incorporating in the mixt. of rubber a pigment prepd. by coating a filling material with a vat dye by oxidation of an alk. soln. or suspension of the vat dye in the presence of the filling agent, the latter being treated with a soap before or after pigmentation. In an example light $MgCO_3$ is heated in a soln. of soap in water, filtered and added to a soln. of the leuco compd. of duranthene blue R. The product is a pigment of considerable strength. Cf. *C. A.* **24**, 1545.

Rubber tires. I. G. FARBENIND. A.-G. Fr. 699,911, Aug. 1, 1930. The different parts of rubber tires are made from polymerization products of butadiene hydrocarbons, the solns. of which have different viscosities. Cf. *C. A.* **24**, 265.

Synthetic rubber. BORIS BUIZOV. Ger. 521,903, Dec. 20, 1927. Synthetic rubber is prepd. by polymerizing butadiene hydrocarbons in the presence of two or more

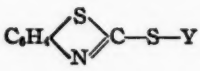
tautomeric substances. Thus, butadiene is polymerized in the presence of diazoaminobenzene and benzoylacetic ester. Further examples are given.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 699,154, July 19, 1930. Masses resembling rubber are prepd. by polymerizing hydrocarbons such as erythrene or its homologs along with mono- or poly-olefinic benzene derivs. such as styrene, divinylbenzene, etc., or their ring or side-chain homologs or by polymerizing mixts. of partially polymerized hydrocarbons with olefinic benzene derivs. Thus, styrene is mixed with twice the amt. of butadiene, emulsified in water and polymerized to give a latex from which a supple rubber is obtained. Other examples are given.

Sheet material suitable for gas receptacles of air craft. WM. C. GEER (to B. F. Goodrich Co.). U. S. 1,801,666, April 21. A thin, flexible sheet of Al or other suitable metal is coated on one side with a tacky rubber isomer and is heated sufficiently to cause flowing of the coating material and to form, when cool, an enamel coating on the Al sheet, and a thin sheet of strong flexible material such as woven fabric is caused to adhere to the coated surface. U. S. 1,801,667 describes bonding metals such as steel, Zn or brass with rubber by applying to the metal surface a thin coherent coating contg. rubber and MgO, heating the coated metal sufficiently to transform the coating of rubber into a relatively dry tough film, coating the film with a rubber cement and vulcanizing a curable rubber compn. in contact with the film. Use of various other substances with rubber also is described.

Factice. JEAN BAER. Ger. 523,210, June 22, 1928. See Swiss 142,354–5–6–7 (*C. A.* **25**, 2332).

Rubber vulcanization accelerators. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,801,764, April 21. A method of treating rubber comprises vulcanizing rubber contg. a metallic oxide and a vulcanizing agent in the presence of a compd. including the group



(Y is, *e. g.*, a trinitrophenyl group); this compd. is capable of hydrolyzing at the S—Y bond in aq. alc. in the presence of NaOH at least as rapidly as diphenylmethyl dimethyldithiocarbamate under the same conditions. Among the compds. of this type, use of which as accelerators is described, are: 2,4,6-trinitrophenyl benzothiazyl sulfide, 2,4-dinitrophenyl benzothiazyl sulfide, picryl benzothiazyl sulfide, 2,6-dinitro-4-chlorophenyl benzothiazyl sulfide, allyl benzothiazyl sulfide, diphenylmethyl benzothiazyl sulfide and phenylmethylenedithiobisbenzothiazole (some of which, however, hydrolyze only slowly, being of very low efficiency as accelerators). Numerous details of procedure and methods of making some of these accelerators are given. U. S. 1,801,765 relates to the use as vulcanization accelerators of triphenylmethyl diethyldithiocarbamate or other triphenylmethyl ester of a substituted dithiocarbamic acid, which ester is capable of hydrolyzing in aq. alc. in the presence of NaOH at least as rapidly as diphenylmethyl dimethyldithiocarbamate. Various details of the use and prepn. of accelerators of this type are given. U. S. 1,801,766 relates to the production, and use as vulcanization accelerators, of 2,6-dinitro-4-chlorophenyl benzothiazyl sulfide and similar compds.

Latex treatment. SIDNEY M. CADWELL and EARDLEY HAZELL (to Naugatuck Chemical Co.). U. S. 1,802,753, April 28. In order to increase the stability and filterability of uncoagulated latex, it is treated with cinnamaldehyde and Na undecylenate, suitably in the proportions of about 1% each. Use of some other similar compds. also is described.

Latex treatment. ROBERT F. ELDER and ROGER B. HILL (to Brown Co.). U. S. 1,804,157, May 5. In a process involving adding creaming and vulcanizing agents to latex, the latex is heated to effect vulcanization while creaming is taking place, and the vulcanized latex is allowed to stand until substantially max. creaming has been effected, and the vulcanized creamed portion of the latex is recovered. Various details of procedure are described.

Conditioning latex. ROGER B. HILL (to The Brown Co.). Can. 311,678, May 26, 1931. A sol. caseinate is added to latex, and then slaked lime is added to ppt. the caseinate and the colloid assocd. with the latex without coagulating the rubber.

Conditioning latex. ROGER B. HILL (to The Brown Co.). Can. 311,679, May 26, 1931. ZnO (5% based on the solids content of the latex) is added to ammonia-preserved latex to effect a reaction on certain of the non-rubber constituents of the latex. The mixt. is heated to 75° for 30 min. and allowed to stand until the excess

ZnO and the reaction products have settled out. The latex is used for impregnating purposes.

Rubber compositions from latex. WILLIS A. GIBBONS (to Naugatuck Chemical Co.). U. S. 1,802,761, April 28. A rubber compn. which has good plasticity and workability is prepd. by mixing a concd. latex, preserved with alkali, with compounding ingredients such as carbon black and clay and evaporating to substantial dryness, and, during these operations and prior to their completion reducing the p_H of the mixt. to not over 7 by mixing it with a material such as H_3PO_4 or a salt which hydrolyzes to give an acid reaction.

Aqueous dispersions containing rubber latex. ARTHUR BIDDLE (to United Products Corp. of America). U. S. 1,802,866, April 28. A compn. suitable for use as an adhesive or binder or for molding, etc., is formed by mixing rubber latex with glue and then adding an insolubilizing agent such as CH_2O to render the glue water-resistant after removal of water from the compn. Fillers, vulcanizing agents, oils, etc., also may be added. Cf. *C. A.* **25**, 3521.

Aqueous dispersions formed with rubber latex and casein, etc. ARTHUR BIDDLE (to United Products Corp. of America). U. S. 1,802,867, April 28. An aq. dispersion is formed from casein, lime, Na_2SO_3 and rubber latex. Use of various other addnl. ingredients also is described.

Aqueous dispersion of rubber. RICHARD A. CRAWFORD (to B. F. Goodrich Co.). U. S. 1,806,388, May 19. At least 4% of an alkali soap of a liquid higher fatty acid such as K oleate is added to a rubber compn. during mastication, and after thorough mastication and while continuing the mastication there is slowly added an aq. NH_3 soln. until the rubber is embodied in the dispersed phase of the batch, and there is then added 1% or more of a nitrogenous protective colloid such as casein and gelatin.

Treating rubber. THE ROESSLER & HASSLACHER CHEMICAL CO. Fr. 700,320, July 24, 1930. The hexamethylenetetraminobenzylic ester of a mercaptothiazole is made by the reaction of the addn. product of a benzyl halide and $(CH_2)_6N_4$ with a salt of a mercaptothiazole, and incorporated in unvulcanized rubber which is then vulcanized. An example is given using the hexamethylenetetraminobenzylic ester of mercaptobenzothiazole.

Rubber treatment. CHARLES E. BRADLEY and CONRAD FERRETTIE (to Mishawaka Rubber and Woolen Mfg. Co.). U. S. 1,805,712, May 19. In order to improve its milling and calendering properties, crude rubber is steeped for about 24 hrs. in water at a temp. of about 65–95°, then treated with steam under 25–50 lb. pressure per sq. in. and dried.

Rubber treatment. CHARLES E. BRADLEY (to Mishawaka Rubber and Woolen Mfg. Co.). U. S. 1,805,713, May 19. Wet rubber is subjected to the action of free O and heated with steam and air under pressure without drying, in order to effect softening for compounding, etc.

Rubber, etc. I. G. FARBENIND. A.-G. Fr. 701,063, Aug. 27, 1930. Rubber, gutta-percha, balata, etc., and products resulting from the polymerization of butadiene hydrocarbons and their transformation products are more easily submitted to mech. treatments such as mixing or kneading after incorporating therewith a lignite wax bleached by oxidizing agents or its transformation products.

Depositing organic materials such as rubber. DUNLOP RUBBER CO., LTD., and ANODE RUBBER CO., LTD. Fr. 700,884, Aug. 19, 1930. The nature of deposits of org. substances such as rubber obtained by electrophoresis of aq. dispersions on cathodic or anodic envelopes is altered by impregnating the envelopes with electrolytes which do not exert a harmful influence on the dispersion and then depositing. The envelopes which may be of porous ceramic materials may be impregnated with a soln. of $Th(NO_3)_4$ or $AlCl_3$ or a soln. of methyl violet or piperidine chloride.

Rubber product. THOMAS MIDGLEY, JR., CHARLES A. THOMAS and CARROLL A. HOCHWALT (to General Motors Corp.). U. S. 1,806,547, May 19. The rubber hydrocarbon is extd. from a natural rubber such as ordinary pale crepe rubber, and this hydrocarbon is compounded with an aminocarboxylic acid such as amino-caprylic acid and with vulcanizing agents, and the mixt. is vulcanized.

Rubber compositions containing clay. WM. FELDENHEIMER. U. S. 1,805,517, May 19. Clay is suspended in water by addn. of Na pyrophosphate in the presence of rosin, any undeflocculated matter is removed, the clay is flocculated from its suspension by the use of a strong acid substance such as $Al_2(SO_4)_3$, and the flocculated product of low acidity is incorporated with a rubber mixt.

Improving resistance of rubber to oxidation. SIDNEY M. CADWELL and LUDWIG MEUSER (to Naugatuck Chemical Co.). U. S. 1,802,752, April 29. Rubber is vul-

canized in the presence of (suitably about 1%) triethanolamine or diethanolamine (or a mixt. of these 2 compds.) as an "age improving material."

Apparatus for molding plastic materials such as rubber compositions. FRANK J. MACDONALD (to B. F. Goodrich Co.). U. S. 1,802,978, April 28. Structural features of an app. suitable for molding rubber heels, etc.

Drum for assembling and curing endless rubber belts. JO D. BERWICK (to Goodyear Tire & Rubber Co.). U. S. 1,805,032, May 12.

Antioxidant. ALBERT M. CLIFFORD (to The Goodyear Tire and Rubber Co.). Can. 311,933, June 2, 1931. Rubber is preserved by subjecting it to vulcanization in the presence of formic acid and a material selected from a group comprising α- and β-naphthylamine. Cf. *C. A.* **25,** 844, 1411.

Rubber articles. THE DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 700,533, Jan. 3, 1930. Homogeneous compns. of rubber, etc., in the flocculent or pulverulent state are made from their aq. dispersions by mixing the aq. dispersions in the presence of one or more colloids under such conditions that the proportion of protective colloids to the components does not give rise to coagulation during the first phases of the operation, but this takes place when a critical proportion is reached. The colloids may be the oleate, stearate or the resinate of NH_4 or alkali metal combinations of higher fatty acids. Cf. *C. A.* **25,** 2021.

Articles formed of fibrous material and rubber. ERNEST HOPKINSON and WILLIS A. GIBBONS (to New York Belting & Packing Co.). U. S. 1,805,245, May 12. In the manuf. of products such as hose, a surface of fibrous material such as a fabric tube is exposed to an aq. dispersion of rubber, and water is continuously withdrawn through the fibrous material until a desired thickness of insol. constituents have been deposited on its surface from the dispersion, and an integral fabric and rubber article is then formed by drying the deposit on the fibrous material. App. is described.

Uniting layers of rubber, fabric and celluloid. WALDO L. SEMON (to B. F. Goodrich Co.). U. S. 1,802,985, April 28. A sheet material comprises celluloid and rubber, attached to opposite sides of a fabric, resp., by a celluloid soln. and by a film of a heat-plastic rubber isomer. Cf. *C. A.* **24,** 265.

Rubber coatings on electric connections, etc. CHARLES R. BOGGS and JOHN T. BLAKE (to Simplex Wire & Cable Co.). U. S. 1,804,199, May 5. A conducting material such as tinned Cu wire is provided with an ozone-resisting coating comprising a body portion of vulcanized gum and a covering of unvulcanized gum of rubber character.

Coating rubber articles with metal. MAX ESCHINGER. Ger. 523,946, Apr. 20, 1929. Rubber articles, especially dental plates, are treated with a solvent and swelling agent, such as di- or trihydroxybenzene, dipped in a soln. of metal salt such as $AuCl_3$, and dried. The dippings may be repeated until a required thickness of salt is deposited. The layer is then reduced to deposit the metal. The metal coating may be reënforced by electrolytic deposition.

Aldehyde-amine condensation products. THE CLAYTON ANILINE CO., LTD. (Rona Robinson, inventor). Ger. 523,694, July 2, 1929. Products *useful in the rubber industry* for preventing aging are obtained by condensing 2 mol. AcH with 1 mol. α-naphthylamine in the presence of an indifferent solvent, and further condensing the product with an aromatic amine. In examples the AcH-naphthylamine product is further condensed with diethylaniline and β-naphthylamine. Cf. *C. A.* **24,** 2008, 4960.

Condensations such as that of oleic acid with α-diethylamino-β-hydroxypropylamine. MAX BOCKMÜHL and ROBERT KNOLL (to I. G. Farbenind. A.-G.). U. S. 1,805,355, May 12. Basic products suitable for use in *prepg. rubber* and as *thickening agents for cosmetics and remedies* are prepd. by heating a compd. of the formula R—CO—X wherein R stands for an aliphatic residue contg. at least 10 C atoms and X for OH, O-alkyl, halogen, NH_2 or an NH_2 group the H atoms of which are substituted by alkyl, aryl or aralkyl, with an amino alc. contg. at least 2 amino groups, one being a tertiary one. Examples are given of the reaction of α-diethylamino-β-hydroxypropylamine with oleic acid, oleic acid ethyl ester and stearic acid amide and of α-diethylamino-β-hydroxy-γ-phenylaminopropane with oleic acid chloride and stearic acid chloride. Cf. *C. A.* **25,** 2253.

Lining for footwear of rubber. CHARLES E. BRADLEY and CLAUDE D. MASON (to Mishawaka Rubber and Woolen Mfg. Co.). U. S. reissue 18,058, May 5. A vulcanized rubber lining is provided with an attached layer of comminuted fibers which do not interfere with the extensibility of the rubber.

Rubber-tire manufacture. LAURITS A. LAURSEN (one-fourth to Pearl L. Laursen). U. S. 1,805,146, May 12. In making a tire of rubber stock and reënforcing cord structure, the cord structure is shrunk, and the stock and cord structure are cured together

while the cord structure is in shrunken condition, to provide reserve stretching capacity for the cord structure.

Polo ball formed with foam rubber. GORDON MEURISSE (to Charles Meurisse & Co.). U. S. 1,803,121, April 28. A ball is formed with a spherical core of foam rubber, in which the d. increases radially inward of the core, and a leather cover around the core.

Coloring thin rubber articles such as toy balloons. ARTHUR P. WITTEN (in part to George E. Hall). U. S. reissue 18,068, May 12. A plurality of the articles are arranged "haphazardly," packed in an enclosed space, and while thus confined are treated with a coloring soln. (Reissue of original pat. No. 1,762,603, issued June 10, 1930.)

Apparatus for reclaiming rubber and fabric from tire beads. MAURICE E. DAVIS (to Leo Meyer Co.). U. S. 1,805,688, May 19. Structural features.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 701,102, July 19, 1930. Masses resembling rubber, which are mixed polymerizates, obtained by polymerizing butadiene hydrocarbons mixed with olefinic benzenes or their homologs or by polymerizing afresh incompletely polymerized hydrocarbons are vulcanized in the presence of finely divided C (lampblack). Examples are given of the prepn. and vulcanization of products from butadiene and styrene or methylstyrene.

Rubber vulcanization accelerator. JULIUS A. NIEUWLAND (to Canadian Electro Products Co.). U. S. 1,804,226, May 5. An accelerator is produced by reaction of C_2H_2 with an amine such as aniline, toluidine or naphthylamine in the presence of Cu_2Cl_2 as a catalyst. Cf. *C. A.* **25**, 1120.

Rubber vulcanization accelerator. JAN TEPPEMA (to Goodyear Tire & Rubber Co.). U. S. 1,805,057, May 12. See Can. 299,953 (*C. A.* **24**, 3135).

Rubber vulcanization accelerators. SIDNEY M. CADWELL and ALEXANDER T. MAXIMOFF (to Naugatuck Chemical Co.). U. S. 1,804,398, May 12. Accelerators are prepd. by causing an aldehyde such as heptaldehyde and a basic nitrogenous material such as aniline to substantially, initially and continuously react with each other at temps. between 100° and 200° (one of the materials being gradually added to the other). Cf. *C. A.* **24**, 4960.

Rubber vulcanization acceleration. DONALD H. POWERS (to E. I. du Pont de Nemours & Co.). U. S. 1,805,103, May 12. Vulcanization is accelerated by the addn. of about 0.5% of the reaction product of 1 mol. of CS_2 and 2 mols. of morpholine (the vulcanization being effected at 20 lbs. steam pressure). Cf. *C. A.* **24**, 266.

Compounding and vulcanizing rubber. WM. A. STEINLE (to Naugatuck Chemical Co.). U. S. 1,802,740, April 28. A suitable dye capable of diffusing into rubber is dissolved in a liquid vulcanizing ingredient having the same diffusing property, and a dispersion is formed also comprising a liquid which does not soften rubber; a rubber compn. is treated with the dispersion so that the dye and vulcanizing ingredient are dispersed into the rubber compn., and the latter is vulcanized. Numerous examples and details of procedure are given.

Apparatus for vulcanizing rubber goods by treatment with steam. THEODORE C. HAZARD. U. S. 1,804,378, May 5. Pressure conditions serve to control the steam supply. Various structural details are described.

"Age-resisting" vulcanized rubber. HORACE G. BYERS (to Rubber Service Laboratories Co.). U. S. 1,806,040, May 19. Before vulcanization, the material is incorporated with a small proportion of *p*-phenylamino-*p*-hydroxydiphenylamine or a similar compd.

Elastic material. RENÉ GIRARD and JULES LEGOUTÉ. Fr. 700,867, Nov. 12, 1929. An elastic material which may replace rubber is made by treating oils, such as colza oil, with chlorides of S, using minium as a catalyst.

Treating latex. JACQUES AUMARÉCHAL and GEORGES ROBRIEUX. Fr. 702,299, Dec. 18, 1929. Powders, pigments, lampblack or various fillers are incorporated in latex to obtain homogeneous pastes by submitting the powders, etc., to the action of steam under pressure with or without NH_3 gas or vapors of aromatic or aliphatic amines or CS_2 or vapors of various oils and afterward grinding them in the concd. or dild. latex.

Treating rubber latex. WILLIS A. GIBBONS (to Naugatuck Chemical Co.). U. S. 1,807,031, May 26. Normal latex is heated to above 100° for 2–3 hrs. without substantial change in its water content, part of the water is removed to form a concd. latex, and the remainder of the water is subsequently removed after fabrication of the concd. latex. Cf. *C. A.* **25**, 3874.

Rubber. I. G. FARBENIND. A.-G. Fr. 701,845, Sept. 10, 1930. The aging of natural and artificial rubber is prevented by adding one or more diaryl- or diarylalkyl- or diaryldialkylmethanes, of which at least one of the aryl groups contains an OH or

alkoxy group and may also contain halogen, NO_2 or an alkyl group. Examples include *o*-hydroxydiphenylmethane, dibenzylphenetole, α-benzyl-β-naphthol, 1,1-di-(*p*-hydroxyphenyl)cyclohexane.

Coloring rubber, etc. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 701,651, Sept. 3, 1930. Articles made from aq. dispersions of rubber, etc., are colored by incorporating in the aq. dispersions one or more compds. capable of producing the desired color after treatment, and treating with a chem. agent or heating to produce the desired color on the surface after the articles are made.

Rubber articles. SOCIETÀ ITALIANA PIRELLI. Fr. 701,406, Aug. 28, 1930. Articles are made from aq. dispersions of rubber, etc., and there are incorporated in the dispersion suitable amts. of alicyclic alcs. obtained by hydrogenating phenols or otherwise, or their oxidation products such as cyclohexanol, cyclohexanone and their homologs. Solns. of soap, saponin or other dispersing substances, and ordinary or concd. or vulcanized latex are also added.

Rubberizing sheet material. THE ANODE RUBBER CO. (ENGLAND), LTD. Ger. 525,444, Jan. 8, 1929. See Brit. 309,391 (*C. A.* **24**, 734).

Rubberized fabric. GEORGE SCHNEIDER (to Camille Dreyfus). Can. 312,236, June 9, 1931. Fabric contg. yarns or org. derivs. of cellulose is rubberized by applying a compn. contg. rubber and S but no pigment or filling material and then vulcanizing the rubber at a temp. above 100°.

Use of *p*-amino-*m*-cresol as an antioxidant in rubber compositions. LUDWIG J. CHRISTMANN (to American Cyanamid Co.). U. S. 1,806,671, May 26.

Rubber tire. ABRAHAM BRILL (to Republic Rubber Co.). U. S. 1,806,838, May 26. The base and tread of a tire are formed of a plurality of grained rubber sections so disposed that all the grain in one section is disposed in planes nonparallel with the plane of the grain of another section.

Rubber tires. RICHARD LIEBAU (to Republic Rubber Co.). U. S. 1,806,857, May 26. Tire treads are formed by folding a strip of rubber back and forth on itself to form a compact assembly of contacting folded portions and then removing the series of turned over edges formed along one edge of the assembly.

Ornamental rubber balls. LEONARD R. HOWES (to Miller Rubber Co.). U. S. 1,806,688, May 26 In making rubber balls with an ornamental veneered surface, a plurality of sheets of thin and thick stock, resp., are thoroughly cooled separately, superposed one on another to produce laminated sheets, and balls are formed from the sheets by joining cupped portions of the laminated sheets.

Improving durability and wearing quality of rubber. WM. P. TER HORST (to Naugatuck Chemical Co.). U. S. 1,807,355, May 26. Numerous examples and details are given of the treatment of rubber or similar vulcanizable materials with a reaction product of an aliphatic ketone and a secondary aromatic amino compd. or a mixt. of such reaction products. Examples of such products are the reaction products of acetone and diphenylamine, acetone and phenyl-α-naphthylamine, acetone and phenyl-β-naphthylamine, acetone and diphenylethylenediamine, acetone and monoethylaniline, methyl ethyl ketone and phenyl-α-naphthylamine, mesityl oxide and phenyl-α-naphthylamine, acetone and diphenylformamidine, mesityl oxide and phenyl-β-naphthylamine, acetone and di-*o*-tolylguanidine, acetone and diphenylguanidine, acetone and *p,p'*-di-(naphthylamino)diphenyl methane, acetone and *o*-tolylbiguanide. The results of using the new antioxidants vary, depending on the ketone and amine used in the reaction. Other ketones than those mentioned that may be used are phorone, diethyl ketone, chloroacetone, dichloroacetone, aldolacetone, biacetyl, acetylacetone, acetonylacetone, diacetone alc., ethylideneacetone, allylacetone, acetophenone, benzalacetone, furfuralacetone, salicylaldehydeacetone, cyclopentanone, cyclohexanone. Other secondary amino compds. than those mentioned that may be used are dinaphthylamines, naphthylaminobiphenyl, carbazole, *p*-nitrodiphenylamine, 2,4-dinitrodiphenylamine, *p*-aminodiphenylamine, *p*-hydroxydiphenylamine, *sym*-diphenyl-*p*-phenylenediamine, *p*-aminobenzylaniline, *p*-amino-*p'*-naphthylaminodiphenylmethane, *sym*-dinaphthyl-*p*-phenylenediamine, phenyl-β-naphthylguanidine, phenyl-*o*-tolylguanidine, di-*o*-tolylbiguanide monophenylbiguanide, diphenylbiguanide. Certain dehydrating agents such as iodine give particularly effective results, but other dehydrating agents may be used such as $CaCl_2$, sulfanilic acid, phosphorus pentoxide, NaOH, $Mg(ClO_4)_2$, HOAc, BaO, $ZnCl_2$, the amine addition product with zinc chloride such as $(C_6H_5NH_2)_2ZnCl_2$, sulfuric acid, silica gel, etc. Use of such compds. retards aging and formation of pinholes or cracks in products such as carbon black tire tread stocks and improves the resistance of the rubber to abrasion. About 1.0–1.5% of the material added for these purposes may suffice.

Rubber substitutes from fatty oils. L. AUER. Brit. 341,490, July 8, 1929. Rub-

ber-like products which can be plasticized on a rubber mill are obtained when fats, fatty oils or esters of their acids are modified, the products emulsified and the emulsions treated as described in Brit. 318,562 (*C. A.* **24**, 2137) with a gas or a modifying agent which yields a gas during the treatment. Non-rubber constituents such as occur in latex are added to the modified fatty substance or to the emulsion, and the precipitatable ingredients are flocculated on the globules of the emulsified fat, in order to make the final product more similar to rubber latex. Proteins, starch or other carbohydrates and stearic acid may be added, and various flocculating agents and details and modifications of procedure are described for making products which can be used for different purposes in a similar manner to natural latex.

Thermoplastic products from thickened fatty oils. L. AUER. Brit. 341,453, July 8, 1929. Thickened fatty oils have dispersed in them, at temps. above 100° (usually about 120–30°, but sometimes up to 250°, and preferably at sub-atm. pressure), modifying agents such as org. metal compds. of the kind mentioned in Brit. 287,943 (*C. A.* **23**, 490), Li_2CO_3 and Li_2SO_3, salts of alkali and alk. earth metals, Zn and Mg with weak acids such as the sulfides, sulfites and carbonates and soaps of these metals, benzenesulfonic acid, 2,5-dichlorobenzenesulfonic acid, *p*- or *o*-nitrophenol, benzenesulfonyl chloride, naphthalene tetrachloride, chlorosulfonic acid in benzene soln., or $Ba(CNS)_2$ dissolved in methyl ethyl ketone. Various examples are given, among which is the treatment of linseed stand oil to form a *vulcanizable "rubber substitute."*

Gutta-percha, balata, etc. WILLOUGHBY S. SMITH, HENRY J. GARNETT and JOHN N. DEAN. Fr. 701,368, Aug. 14, 1930. Gutta-percha, balata and like modified natural gums are produced by selectively extg. the resins so as to leave in the mass that of the type of alban, the fluavil and like resins being removed. Alc. or ketones are suitable solvents. Cf. *C. A.* **25**, 618.

Embossing vulcanized sheet rubber. ROLAND G. ANDERSON (to Wellman Co.). U. S. 1,807,024, May 26. Mech. features.

Washing out used vulcanization molds. "HEROLD" A.-G. Ger. 525,163, Dec. 6, 1927. Solns. of sugar-like substances are used, *e. g.*, a soln. of cane sugar 1, with or without dextrin 0.5, in water 100 parts.

Vulcanizing rubber articles. THE GOODYEAR TIRE & RUBBER CO. Ger. 525,445, Mar. 3, 1928. See Brit. 288,248 (*C. A.* **23**, 732).

Aqueous dispersions suitable for treating rubber latex. A. SZEGVARI (to Dunlop Rubber Co., Ltd. and Anode Rubber Co., Ltd.). Brit. 342,194, April 20, 1929. Dispersions such as those of a resinous condensation product of AcH and aniline or of aldol with α-naphthylamine, tar or "mineral rubber" or petrolatum are prepd. by dissolving the materials in "rubber oil" (obtained by dry distn. of rubber or the like) and then emulsifying with water and various usual emulsifying agents. Several examples with details are given.

Separating and curing constituents of sapotaceous gums such as balata and gutta-percha. FELIX F. VON WILMOWSKY. U. S. 1,808,191, June 2. A process is described which consists in (1) dissolving the gum hydrocarbons in a suitable solvent such as warmed or heated volatile petroleum; (2) gradually pptg. the gum hydrocarbons by means of gradually changing phys. factors such as running time and gradual lowering of the temp. of the soln., removing the gum hydrocarbon portions as they gradually ppt. one after the other and preferably selecting and compounding some of the sepd. grades or lots of gum hydrocarbons in certain proportions; and (3) curing or vulcanizing the gum hydrocarbons. Sepd. pure gums substantially free from resin, when cured (*e. g.*, with "pentasulfide of hydrogen") yield products similar to high-grade rubber. Various details of app. and procedure are described.

Carbon black. WM. B. WIEGAND. U. S. 1,807,884, June 2. The properties of impingement C blacks for use in rubber compns. are improved by calcining in a non-oxidizing atm. at a temp. not less than about 650°. App. is described.

Antioxidants. ALBERT M. CLIFFORD (to Goodyear Tire Rubber Co.). Can. 313,060, July 7, 1931. Rubber is preserved by vulcanizing in the presence of a reaction product of β-naphthol, CH_2O and an amine selected from a group comprising aniline, toluidine and naphthylamine. Cf. *C. A.* **25**, 3875.

Rendering rubber "age-resistant." ALBERT M. CLIFFORD (to Goodyear Tire & Rubber Co.). U. S. 1,809,798, June 9. The product of reaction of β,β-dinaphthylamine and S (effected with elimination of H_2S, suitably at a temp. of about 180–190°) is incorporated with the material as a preservative. U. S. 1,809,799 relates to the use for the same purpose of compds. such as 3-β-naphthylaminoacenaphthene.

Preserving rubber with halogen-substituted diarylamines such as *p*-chlorophenyl-β-naphthylamine. WALDO L. SEMON (to B. F. Goodrich Co.). U. S. 1,808,578, June 2. About 0.5% may be added to a rubber compn.

Rubber articles. DUNLOP RUBBER CO., LTD. and THE ANODE RUBBER CO., LTD. Fr. 702,465, Sept. 23, 1930. Articles exclusively or partially of rubber are made by covering supports or supporting layers with aq. dispersions or emulsions previously acidified and of acid reaction, and afterward covering the supports or supporting layers thus treated with the principal emulsions or dispersions.

Apparatus for manufacturing and stretching endless rubber belts. RAY M. JOHNSON (to Goodyear Tire & Rubber Co.). U. S. 1,809,803, June 9. Mech. features.

Manufacture of hose of rubber and fabric. LOUIS H. GLADWIN and NIGEL G. BRUCE (to Goodyear Tire & Rubber Co.). U. S. 1,809,802, June 9. Various details of app. and operation are described.

Depositing rubber. SIEMENS-ELEKTRO-OSMOSE G. M. B. H. (Nikolaus Schönfeldt, inventor). Ger. 526,303, Mar. 16, 1928. The electroösmotic deposition of rubber from latex is effected in a cell divided into an anode and a cathode compartment by a diaphragm on which the rubber is deposited. One compartment contains latex, and the other contains a practically anhyd. dielec. liquid, *e. g.*, transformer oil. A d. c. of high p. d. is used. The diaphragm may consist mainly of powd. Cr_2O_3.

Rubber coatings on metal. THE ANODE RUBBER CO., LTD. Ger. 524,752, Feb. 7, 1929. Rubber coatings on metal, deposited by brushing on, spraying, etc., are caused to adhere by giving the coating an under-layer of gauze or mesh. Cf. *C. A.* **24**, 1765.

Chlorinated rubber solutions. NORRIS BOEHMER. U. S. 1,807,616, June 2. Chlorinated rubber is washed to remove some of the water-sol. impurities, and is then dissolved in a solvent such as a mixt. of about equal parts of Me_2CO and an aromatic hydrocarbon such as C_6H_6. The soln. is treated with quicklime in order to produce a clear soln. free from HCl.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 702,784, Sept. 30, 1930. Diolefins are polymerized in the presence of alkali or alk. earth metals, their mixts. or alloys and in the presence of small quantities of halogenated org. compds. Examples are given of the use of 1,2-dibromocyclohexane, α-chloro- and α-bromo-naphthalene, chloroquinaldine, vinyl chloride, $C_6H_5CH_2Cl$ and others.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 342,314, Aug. 30, 1929. In a process as described in Brit. 339,255 (*C. A.* **25**, 2598), in which a diolefin is polymerized in the presence of styrene, the latter is replaced by other olefin benzenes such as polyvinylbenzenes, contg. 2 or more vinyl groups attached to a benzene nucleus, or nuclear or side-chain homologs of these or of styrene; *e. g.*, butadiene and α-methylstyrene may be formed into an aq. emulsion with an admixt. of diethylaminoethyloleamide and polymerization effected with agitation at a temp. of about 60° for 4–5 days.

Catalysts for producing synthetic rubber from diolefins. I. G. FARBENIND. A.-G. Brit. 342,107, Jan. 9, 1929. A catalyst for polymerizing diolefins is prepd. by grinding Na with a diluent such as dry NaCl in an atm. of N.

Rubber-like product. JEAN BAER. Ger. 526,121, June 30, 1928. See Swiss 142,456 (*C. A.* **25**, 2332).

Rubber substitutes. I. G. FARBENIND. A.-G. (Hans Lecher and Albert Koch, inventors). Ger. 526,304, Mar. 17, 1928. In the manuf. of rubber-like products by polymerizing emulsified diolefins, the emulsions are homogenized before polymerization. Examples are given.

Rubber substitutes. I. G. FARBENIND. A.-G. (Otto Ambros and Hans Reindel, inventors). Ger. 526,305, Aug. 26, 1928. Emulsified diolefins are polymerized in the presence of polymerized castor oil or its derivs. Examples are given.

Rubber substitutes. I. G. FARBENIND. A.-G. (Hans Lecher and Albert Koch, inventors). Ger. 526,498, Mar. 18, 1928. A substance promoting emulsification is dissolved in butadiene or a homolog or analog thereof, and the soln. is emulsified with an aq. soln. of another substance promoting emulsification. The resulting emulsion is polymerized, with or without preliminary homogenization. Examples are given.

Vulcanizing accelerator. JAN TEPPEMA (to Goodyear Tire & Rubber Co.). U. S. 1,809,457, June 9. See Can. 300,808 (*C. A.* **24**, 3925).

Aldol condensation products as rubber vulcanization accelerators. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,809,454, June 9. As accelerators there are used reaction products of acetaldol and NH_3, ethylenediamine, allylamine, butylamine, diethylamine or dibutylamine.

Curing rubber articles such as tires. HENRY R. MINOR (to Liquid Carbonic Corp.). U. S. 1,808,428, June 2. An expansible bag is placed adjacent to the articles and is filled with CO_2 to produce initial pressure; the initial pressure is backed up by steam. App. is described. Cf. *C. A.* **24**, 3399.

Heat-transfer system suitable for use in curing rubber tires. HENRY R. MINOR

(to Liquid Carbonic Corp.). U. S. 1,808,429, June 2. Various details are given relating to the use of CO_2 with steam.

Apparatus for vulcanizing articles such as tires by heating. HAROLD A. DENMIRE (to General Tire & Rubber Co.). U. S. 1,808,711, June 2. Structural features.

Vulcanizing apparatus. ALAJOS PAUER. Hung. 102,572, April 19, 1930. Mechanical features are described.

Mold-cleaning solution. RALPH C. BATEMAN (to Goodyear Tire & Rubber Co.). Can. 313,061, July 7, 1931. Rubber vulcanization molds are cleaned by heating them in the presence of a soln. of cresol in an oil derived from pine wood.

Reclaiming vulcanized rubber. MORRIS OMANSKY (to Arthur D. Little, Inc.). U. S. 1,807,930, June 2. The material is digested with an alkali such as NaOH capable of destroying the fabric and plasticizing the rubber, washed to remove alkali, dried and mixed with a small proportion (suitably about 1%) of an acid reagent contg. the SO_4 radical such as 66° Bé. H_2SO_4. HNO_3, chromic acid, $NaHSO_4$ or $(NH_4)_2SO_4$ also may be added.

Reclamation of rubber. ARTHUR E. BARNARD (to The Dispersions Process, Inc.). Can. 312,800, June 30, 1931. Vulcanized rubber is plasticized and dispersed in water contg. rosin soap, and $Al_2(SO_4)_3$ is added to flocculate the rubber. The rubber flocs are screened out, washed and dried.

Treating latex. H. C. HOWARD (to Anode Rubber Co., Ltd.). Brit. 341,744, March 8, 1929. Latex (or various similar natural or artificial dispersions) is treated with an adsorbent agent such as silica gel, activated C or colloidal Al_2O_3, to reduce its alky. (the adsorbent being prepd. for use by heating at about 105° for an hr. to remove previously adsorbed substances), and the adsorbent is substantially removed from the latex before its use for dipping or other operations.

Concentrating latex. K. D. P., LTD. Brit. 341,677, Dec. 19, 1928. In producing a reversible concentrate from latex, K salts of hydrotropic substances (excepting K soaps and K salicylate) are used as protective substances, and for this purpose there may be used: K 2,3-hydroxynaphthoate, K 2,1-hydroxynaphthoate, the K salt of Turkey-red oil, the K salt of sulfanilic acid or K *o*-hydroxyquinolincarboxylate.

Rubber. HERMANN BECKMANN. Fr. 37,521, Oct. 21, 1929. Addn. to 606,989. See Brit. 338,698 (*C. A.* **25**, 2597). Rubber with microscopical pores is obtained by adding to rubber latex a substance which can be coagulated and the gel of which fixes water. The liquid is treated with a coagulating agent which acts on the added substance and on the latex. The product is vulcanized in known manner. Suitable addns. to the latex are SiO_2, stannic acid, $Al(OH)_3$, colloidal Fe_2O_3, albuminoids, hemoglobin, etc.

Transformation products of rubber. I. G. FARBENIND. A.-G. Fr. 704,757, Oct. 30, 1930. Natural rubbers or their suspensions or solns. are treated with mixed org.-inorg. oxonium compds. obtained by combining Al halides, $SnCl_4$ or concd. H_2SO_4 with halides or anhydrides of carboxylic acids or with other org. compds. such as ethers or ketones (not aldehydes). The products when vulcanized are resistant to friction. In an example phthalyl chloride and $AlCl_3$ are added to a soln. of rubber in C_6H_6. The product is pptd. by EtOH. Other examples are given.

Coloring rubber and similar materials. DUNLOP RUBBER CO., LTD., R. G. JAMES and D. F. TWISS. Brit. 344,537, Dec. 12, 1929. For coloring articles of rubber, gutta-percha or balata produced from aq. dispersions, by use of org. sol. dyes the cations of which are colored, the charge on the particles of the dispersions is inverted from neg. to pos. prior to admixture with the dye. For this purpose there may be added an acid or a salt with a multivalent cation such as Th nitrate. Cellulose esters or ethers or protein material such as casein may be present in the dispersions. Cf. *C. A.* **25**, 4149.

Colored rubber. THE FLINTKOTE CO. Fr. 704,805, Oct. 31, 1930. Colored rubber is made by incorporating appropriate vegetable or animal fibers in vulcanized or unvulcanized rubber, which may be in the form of a dispersion, soln. or plastified mass. The mass is given the desired form and then treated with a coloring substance so that the fibers absorb the color.

Reconditioning old rubber. F. J. CLEVELAND. Brit. 340,985, Aug. 7, 1929. The finely divided material is incorporated with about 5% of S and then treated with a liquid mixt. contg. benzene 4, CS_2 1 and CCl_4 1 dram per pound of rubber. Fillers, "antiagers," accelerators and raw crumb rubber also may be added.

Regenerating rubber. HELSINGBORGS GUMMIFABRIKS AKTIEBOLAG. Fr. 703,660, Oct. 13, 1930. Vulcanized rubber is regenerated in known manner with Hg or a Hg compd. as catalyst. The amt. of Hg used is about 0.5% of the wt. of the rubber.

Using waste rubber. OSCAR C. HOSKING. Fr. 704,843, Oct. 31, 1930. Waste rubber is broken up and added to fresh or unvulcanized rubber dispersed in a volatile

agent such as benzine. The mixt. is spread out in a ventilated chamber from which actinic light rays are excluded, and allowed to dry at about 85°. The spongy mass obtained may be used for soles of shoes, floors, etc. If a better product is desired the spongy mass is submitted to the action of heat (110–126°) under pressure.

Rubber compositions. I. G. FARBENIND. A.-G. Brit. 341,258, Jan. 9, 1930. Addn. to rubber of 2–10% of montan wax bleached by oxidation or a conversion product (suitably with conjoint addn. of about half the quantity or less of stearic acid) facilitates mixing with addnl. substances such as vulcanizing agents, accelerators, fillers, coloring substances, etc. Larger quantities of wax (up to 4 times the wt. of the rubber) form thermoplastic products. Various details and examples are given, including also the use of synthetic rubber and balata. Cf. *C. A.* **25**, 2020.

Rubber compositions for tires. I. G. FARBENIND. A.-G. Brit. 340,681, Oct. 30, 1929. In the use of plastic products obtained by the polymerization of butadiene, as described in Brit. 299,037 (*C. A.* **23**, 3376), for tire manuf., solns. of these products of like concn. in the same solvent but of different viscosities are used for the different parts of the tire such as the side walls and the tread (a higher viscosity is usually employed for the tread portion). Numerous details of sp. mixts. used are described.

Rubber tires. I. G. FARBENIND. A.-G. Fr. 37,663, Nov. 29, 1929. Addn. to 660,634 (*C. A.* **24**, 265). The frame of road tires is made of rubber and the surface in contact with the road is made of the polymerization products of butadiene hydrocarbons which do not distil without decompn. Cf. *C. A.* **25**, 3521.

Rubber compositions for playing ball cores and covers. R. C. SWABEY. Brit. 341,566, Oct. 24, 1929. A core compn. formed of rubber, PbO, cottonseed oil and S is molded under heat and pressure and semi-vulcanized. Hemispherical cover shells may be formed of a mixt. of rubber, gutta-percha or balata, china clay, S and an accelerator. For a golf ball, a winding of rubber thread is placed between the core and cover.

Rubber composition horse shoes. N. KENYON and SPEN RUBBER WORKS, LTD. Brit. 344,586, Jan. 8, 1930. A vulcanized compn. having some of the characteristics of wood may be formed of rubber 2, wood flour 20 and S 6 parts. Various structural features are described.

Rubber composition or "artificial leather." O. G. BOHLIN. Brit. 340,305, Sept. 25, 1929. Rubber is mixed with ground herbaceous vegetable material such as straw powder in about equal proportions by wt. without use of a solvent.

Waterproof imitation leather. ZISEKI NÔTA. Japan 90,527, Mar. 2, 1931. Cotton material is immersed in a mixt. of latex, ZnO, S and vulcanization accelerator and pressed on a heated roll. The material is then vulcanized by applying heat to the roll.

Molding rubber footwear. H. C. L. DUNKER. Brit. 341,439, Oct. 3, 1929. In making boots or shoes or the like, rubber is pressed between movable outer molds and a hollow last previously covered with the necessary layers of fabric and rubber (the last being inflatable to effect the molding). Cf. *C. A.* **25**, 2332.

Articles from dispersions such as those of rubber. GEORGE G. THORNTON (to American Anode, Inc.). U. S. 1,810,504, June 16. For producing irregular markings on the surface of tobacco pouches or other rubber articles, a rubber deposit is formed from an aq. dispersion of rubber, the deposit is dried, the dried deposit is confined between suitably shaped plates, and the deposit and plates are immersed together in a heated liquid such as hot water.

Surfacing rubber with halogenated rubber. BENJAMIN S. GARVEY (to B. F. Goodrich Co.). U. S. 1,810,560, June 16. A vulcanized surface such as that of soft rubber is subjected to halogenation, such as chlorination, and a layer of halogenated rubber is applied to the surface (suitably by use of a soln. comprising rubber chloride and *o*-nitrodiphenyl ether). Surfaces thus prepd. are resistant to hydrocarbons, acids, etc.

Porous rubber sheet for use in flotation or other aeration treatments of liquids. W. T. MACDONALD (to F. P. Egeberg). Brit. 344,238, March 18, 1929. Structural features.

Electric insulating plate. YOSIO NIWA and USIMATU NAKAGAKI. Japan 90,553, Mar. 3, 1931. A mixt. of powdered cork, raw rubber, lime, S and paraffin is pressed and heated, by which the rubber is vulcanized. The plate is flexible.

Accelerator for the vulcanization of rubber. THE RUBBER SERVICE LABORATORIES Co. Fr. 704,661, Oct. 21, 1930. An aldehyde is combined with the reaction product of an aromatic amine and a mercaptoarylthiazole. Thus, the compd. obtained by heating mercaptobenzothiazole with 2,4-diaminodiphenylamine is treated with AcH. Other examples are given, and examples of the use of the compds.

Vulcanizing rubber. I. G. FARBENIND. A.-G. Fr. 703,791, Oct. 17, 1930. Prod-

ucts resulting from the oxidation of paraffin or waxes other than lignite wax, freed from resin and asphalt, or the acid components sepd. from the oxidation products, or the Zn salts of these products, are used in the vulcanization of natural or synthetic rubber. Cf. *C. A.* **25**, 3200.

Vulcanizing tires. SOCIETÀ ITALIANA PIRELLI. Brit. 341,143, Oct. 23, 1928. Tire casings are shaped and consolidated by heat and pressure (suitably in an ordinary vulcanizing mold), then removed and vulcanized, or the vulcanization is completed by heating them in water under a pressure higher than that of satd. steam at the vulcanizing temp. Compressed air may be used to increase the pressure on the water.

Rubber vulcanization acceleration. NAUGATUCK CHEMICAL CO. Brit. 340,573, July 1, 1929. Vulcanization is accelerated, without danger of scorching, by use, together with a metal oxide such as ZnO, of a compd. including the group RCS(:X)Y, in which R represents N, O or C, and X represents O or S, such as dithiocarbamates, xanthogenates and dithiobenzoates (R and X may also be members of a thiazole ring) and Y represents C in a substituted cyclic or methyl group which does not contain O or S doubly bonded to Y (the compds. used hydrolyze at the SY bond in aq. alc. in the presence of NaOH at least as rapidly as diphenylmethyl dimethyldithiocarbamate). The prepn. of suitable accelerators is described in Brit. 340,574, and among the compds. which may be used are: polynitro aryl esters of substituted dithiocarbamic acid having at least one nitro group *ortho* to the 1-position and one of the remaining groups *meta* to the nitro group, and phenylmethylenebis esters of alkyl dithiocarbamates. Acceleration may be increased by adding NH_3 or retarded by adding acids. Treating substances may be introduced by diffusion and various details and examples are given. Cf. *C. A.* **25**, 3522.

Sectional drum for vulcanizing endless belts. J. D. BERWICK (to Goodyear Tire and Rubber Co.). Brit. 340,773, April 16, 1929. Details of a drum built up of telescoping cylindrical sections.

Rubber. ROBERT M. WITHYCOMBE. Ger. 526,863, Dec. 3, 1925. Rubber is jointed to metals by coating the metal with a mixt. of powd. wood charcoal, NaCl, rubber and gutta-percha dissolved in C_6H_6, $CHCl_3$, etc.

Rubber. DEUTSCHE GASGLÜHLICHT-AUER-G. M. B. H. Ger. 526,864, Oct. 26, 1927. Rubber is vulcanized by addn. of up to 80% TiO_2 and treating the mixt. with SCl_2 or S_2Cl_2 vapor.

Rubber compositions. THE BARRETT CO. Ger. 529,054, Dec. 3, 1925. See Brit. 243,384 (*C. A.* **20**, 3842).

Rubber articles direct from latex. TULLIO G. LEVI (to Società italiana Pirelli). U. S. 1,811,695. June 23. See Brit. 335,621 (*C. A.* **25**, 1705).

Rubber products with lustrous surface. KUMEITU MORIMOTO, SEIITI SANO and TUTOMU SANO. Japan. 90,923, April 6, 1931. A mixt. of nitrocellulose, camphor, castor oil, solvents and tetralin or cyclohexanol is painted on a rubber compn. such as a mixt. of raw rubber, S, vulcanization accelerator, etc. The whole is heated for vulcanization. The surface is lustrous.

Mold-filling apparatus suitable for use in manufacture of rubber heels. JOHN R. GAMMETER. U. S. 1,811,430, June 23. Structural features.

Apparatus for forming cylindrical blanks for manufacture of inner tubes. HARRY C. BOSTWICK (to Akron Standard Mold Co.). U. S. 1,811,453, June 23. Structural features.

Marking rubber cords and cables. GEORGE J. CROWDES (to Simplex Wire and Cable Co.). U. S. 1,812,686, June 30. A Pb jacket is formed on the rubber with a groove in its inner side and a marking ribbon therein, the jacketed rubber element is vulcanized, and the jacket is then stripped off. App. is described.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 340,474, Aug. 19, 1929. Polymerization of diolefins by use of metals or alkali metal hydrides or organometallic compds. is facilitated by adding org. compds. of the general type $Me.(diolefin)_z.Me$ or $R.(diolefin)_z.Me$ with the replacement of the metal atoms in these org. compds. by H atoms or org. groups, and which do not react, or react but slowly, with alkali metals. These org. compds. react in a similar manner with triphenylmethyl Na, and the latter can be used in detg. the suitability of an org. compd. for use as a regulator of the polymerization (in a color test which is described). Numerous substances are mentioned as suitable for use such as allyl ether, ethylpropenyl ether, ethyl propargyl ether, vinylethyl,-isopropyl and -butyl ethers, α-phenylvinyl ethyl ether, vinyl *m*-cresyl ether, vinyl *o*-cresyl ether, vinyl-α-naphthyl ether, vinyl β-naphthyl ether and ethyl cyclohexenyl (2,3) ether, thiophene, thionaphthene, allyl sulfide and allyl mustard oil. Polymerization products are obtained which may be used for the manuf. of artificial silk, artificial wool, coatings, films, etc. A soln. of triphenylmethyl Na in ether is prepd. by action

of Na amalgam on triphenylchloromethane in a sealed tube from which air is excluded (with agitation for 12 hrs.).

Aldehyde-amine condensation products. THE CLAYTON ANILINE CO., LTD. Ger. 529,320, July 30, 1929. See Brit. 326,525 (*C. A.* **24,** 4960).

Rubber vulcanization accelerators. NAUGATUCK CHEMICAL CO. Brit. 340,951, July 1, 1929. Thioethers of aryl thiazoles, suitable for treatment of rubber as described in Brit. 340,573 (*C. A.* **25,** 4742) are prepd. by treating an aryl mercaptothiazole salt with a halonitroaryl compd. or an aryl or alkyl substituted methyl halide. Among the products which may be thus formed are: 2,4-dinitrophenyl-, 2,4,6-trinitrophenyl- and 2,6-dinitro-4-chlorophenyl-thioethers of benzothiazole and the diphenylmethyl-, triphenylmethyl-, benzal-*bis*-, tertiary butyl- and allyl-thioethers of benzothiazole.

Rubber vulcanization accelerators. NAUGATUCK CHEMICAL CO. Brit. 340,574, July 1, 1929. Accelerators are described comprising dithiol esters which may be produced by treating a dithiocarbamate, xanthogenate or aryl dithiocarboxylate salt with a halogen-substituted nitroaryl compd. or an aryl or alkyl substituted methyl halide (of which numerous examples are given), and the use of which in rubber vulcanization is also described in Brit. 340,573 (*C. A.* **25,** 4742).

Apparatus for vulcanizing tires. KARL B. KILBORN (to Seiberling Rubber Co.). U. S. 1,812,792, June 30. Structural features.

Apparatus for vulcanizing inner tire tubes, etc. ERNEST BLAKER (to B. F. Goodrich Co.). U. S. 1,812,282, June 30. Structural features.

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Some Fundamental Rubber Problems

G. Stafford Whitby

In a famous phrase Kipling once declared: "What do they know of England who only England know!" If I may take the liberty of paraphrasing this, I would ask: What do they know of rubber who only rubber know? I believe that it is a mistake, particularly in regard to the more fundamental problems presented by rubber, to direct attention too exclusively to rubber itself, and that it is highly desirable and indeed almost essential to consider other materials which display in some degree the behavior and properties of rubber. By drawing analogies from the study of simpler and more tractable systems, we may hope to obtain an insight into the more complicated and difficult case of natural rubber itself. It is my intention to offer some considerations regarding the chemical constitution of rubber, approaching the question from a consideration of the mechanism of polymerization in general; regarding the physical structure of rubber, approaching the question from a consideration of the behavior of artificial elastic colloids; regarding the nature of vulcanization, approaching the question from a consideration of the vulcanization, not of rubber, but of fatty oils.

Chemical Constitution of Rubber

Starting from the premise that rubber is a polymer of isoprene, it would seem possible to arrive at some conclusions as to the chemical constitution of rubber by considering the way in which polymerization in general proceeds, and then applying the general conclusions to the case of the polymerization of isoprene.

The first general question to be considered regarding polymerization is whether the union of a large number of molecules of the monomer, to yield in many cases a product with colloidal properties, is due to primary chemical valencies or to secondary molecular forces. In the case of the polysaccharides, such as cellulose, the most generally, though by no means universally, accepted view is that "polymerization" and the appearance of colloidal properties are due to secondary forces. The case of cellulose is not, however, necessarily analogous to that of a hydrocarbon such as rubber, or to other typical polymers. In the first place, there are oxygen bridges in cellulose—and oxygen is well known to be capable of exhibiting auxiliary valencies. In the second place, cellulose, $(C_6H_{10}O_5)n$, is not, so far as is known, a polymer at all in the sense that it is derived from a monomer, $C_6H_{10}O_5$, of the same empirical formula; it is, rather, a condensation product of a number of hexose molecules. In typical cases of polymerization the monomeric molecules which become united in order to build up the polymer contain an unsaturated center, such as C:C, C:O, or C:N. So far as is known, cellulose is not derived from a monomeric molecule, $C_6H_{10}O_5$, containing any such grouping. It can hardly be regarded as a typical polymer.

In the case of an unsaturated polymeric hydrocarbon such as rubber, it is natural to suppose that, if the polymerization and the possession of colloidal properties are due to secondary valency forces, such forces must be associated with the unsaturated centers in the molecule. Yet, as Pickles (*J. Chem. Soc.*, **97**, 1085 (1910)) long ago pointed out, these centers can be saturated without causing the rupture of the

polymeric aggregate into small units devoid of colloidal properties. Pickles pointed out that if the double bonds of rubber are saturated with halogens or halogen hydrides the products still possess colloidal properties. They show also elastic properties when warmed (Whitby, *Colloid Symposium Monograph*, **1926**, IV, 203). In this connection it may be noted that the open-chain polyterpene, squalene, $C_{30}H_{50}$, a hydrocarbon closely related to an open-chain polymer of isoprene (*vide infra*), yields a *crystalline* dodecabromide (Staudinger and Fritschi, *Helv. Chim. Acta*, **5**, 785 (1922)). Were rubber, as has recently been suggested, a relatively small "chemical" molecule, $C_{40}H_{64}$, "aggregated" by means of secondary forces, it would be expected, by analogy, that, on adding bromine and thus causing the disappearance of the unsaturated centers with which the secondary forces would be associated, the product, $C_{40}H_{64}Br_{16}$, would similarly be crystalline. In point of fact, it is colloidal.

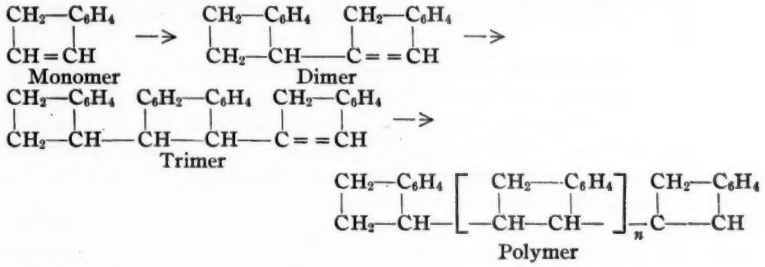
In recent years Staudinger has produced a variety of massive evidence on similar lines in favor of the view that primary valencies are concerned in uniting simple molecules to form high polymers. He has shown that the double bonds of rubber can be satisfied with hydrogen without loss of colloidal properties (Staudinger and Fritschi, *loc cit.*); that rubber hydrobromide on treatment with zinc ethyl yields a saturated hydrocarbon, ethyl hydrorubber, without rupture of the aggregate (Staudinger and Widmer, *Ibid.*, **7**, 842(1924)). He has adduced numerous other cases in which a polymeric, colloidal product goes through a series of chemical reactions as a unit, without breakdown to the monomer or other simpler unit. For example, polymerized acrylic acid can be converted into polymerzied methyl acrylate; the latter on treatment with methyl magnesium iodide yields a polymerized tertiary alcohol which can be reduced to a polymerized saturated hydrocarbon (Staudinger, *Ber.*, **59**, 3019 (1926)). It is difficult to believe that polymerized products could undergo such various chemical transformations as those just instanced, without the disappearance of the polymerized condition, if the latter were not due to primary valencies. Another case which might be quoted in this connection is polyvinyl acetate, which on saponification yields polymerized vinyl alcohol.

The case of polymerized styrene (metastyrene) is worth consideration. In the polymerization of styrene, unlike that of isoprene, all ethylenic linkages disappear, and the product is (except for the benzenoid rings) a saturated hydrocarbon; yet it shows colloidal and elastic properties similar to those shown by rubber (Whitby, *Colloid Symposium Monograph*, **1926**, IV, 203. And Staudinger has shown that even the benzene rings in metastyrene can be fully hydrogenated without rupture of the molecule into small units (Staudinger, Geiger, and Huber, *Ber.*, **62**, 263 (1929)).

In a lecture recently delivered before this Section, Auer (*Trans. Inst. Rubber Ind.*, **4**, 499 (1929)) contrasted metastyrene and distyrene, describing the former as an "aggregated" product and the latter as a true polymeric product, the implication being that, whereas in the formation of distyrene true chemical union of styrene molecules takes place, in the formation of metastyrene "a type of coagulation" occurs, the molecules of styrene being united by means, not of primary valencies, but of "colloidal forces." Disproof of this conception is, however, to be found in a study of the pyrogenic decomposition of metastyrene, for the latter yields on distillation under reduced pressure distyrene itself (and also tristyrene) (Whitby and Katz, *unpublished*).

Indene yields a series of polymers ranging up to products of high molecular weight, the investigation of which does not present such great difficulties as does that of the polymeric products from isoprene, styrene, etc.; and their study has

enabled a picture of the mechanism of polymerization to be drawn clearer probably than any previously available (Whitby and Katz, *J. Am. Chem. Soc.*, **50**, 1160 (1928)). Although the polyindenes are not, except in the lowest members of the series, crystalline, they do not, like rubber and metastyrene, yield highly viscous solutions, and hence molecular weight determinations are less affected with uncertainty, and, further, mixtures of polyindenes can be split up into close fractions, representing approximately chemical individuals, in a way that is not possible with the less tractable, lyophilic polymers just mentioned. A series of polymeric products can be isolated, ranging from one, representing the union of two, to one representing the union of thirty or more molecules of indene. All these products, no matter what their molecular weight, contain one double bond per molecule, as shown by the fact that all absorb two atoms of bromine per mole. It appears to be beyond question that the polyindenes are built up by the addition of successive molecules of indene to the previous stage or of the previous polymeric stage to successive molecules of indene, as shown in the following scheme:



The last represents the general formula of all the polyindenes, where n ranges from 0 to 28 or more.

Such a scheme of polymerization is, I believe, typical of cases where unsaturated compounds are capable of giving rise to high molecular polymers. The process represents a succession of additions of a regular chemical character to the double bond of the monomer or of the previous polymeric stage, an atom of hydrogen wandering to one side of the double bond and the rest of the addendum going to the other side. Each stage in the polymerization process represents a definite chemical individual.

When polyindenes are subjected to pyrogenic decomposition under reduced pressure, as in the case of metastyrene (*vide infra*), the molecular chain splits at a number of different points and there distil over mono-, di-, tri-, and tetraindenes, the nondistillable residue consisting of a mixture of polyindenes, higher than tetraindene but lower in molecular weight than the original material (Whitby and Katz, *unpublished*). The ease of cracking is, as has also been found to be the case with metastyrene, greater, the larger the molecule of the specimen of polyindene in question.

If the polymerization of isoprene takes place according to a scheme similar to that just posited for the polymerization of indene, then rubber is to be regarded as an open-chain terpene of high molecular weight. In this case, unfortunately, the behavior on pyrogenic decomposition under reduced pressure is not so simple as in in the case of saturated (or substantially saturated) polymers such as metastyrene and the higher polymers of indene. Owing to the occurrence of a double bond at every fourth position in the chain, cyclization takes place, and, with the exception of a small amount of isoprene, it is not possible to distil over the fragments into

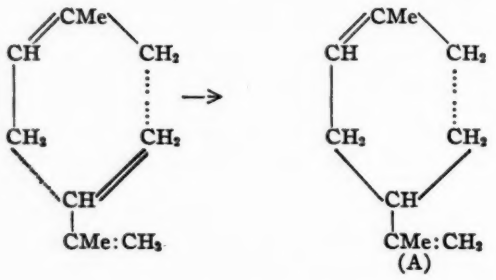
which the chain originally splits, the main products being cyclic terpenes (cf. *e. g.*, Fischer and Harries, *Ber.*, **35**, 2158 (1902)). That cyclization occurs during the pyrogenic decomposition of high open-chain terpenes is made particularly clear by the recent observations of Heilbron and his collaborators (Heilbron, Kamm, and Owens, *J. Chem. Soc.*, **1926**, 1630; Harvey, Heilbron, and Kamm, *Ibid.*, 3136) on the pyrolysis of the dihydrotriterpene, squalene. Squalene appears to consist mainly of the following hydrocarbon, which can be regarded (Heilbron, Owens, and Kamm, *loc. cit.;* Heilbron, Ownes, and Simpson, *J. Chem. Soc.*, **1929**, 873; Heilbron and Thompson, *Ibid.*, 883) as a dihydro open-chain hexamer of isoprene, *viz.*:

$$CH_3.CMe{:}CH.CH_2.[CH_2.CMe{:}CH.CH_2]_4.CH_2.CMe{:}CH.CH_3$$

and it has been found to behave on pyrolysis in a way very reminiscent of the behavior of rubber, yielding amylene, and cyclic mono-, sesqui-, di-, and probably even higher terpenes (Heilbron, Kamm, and Owens, *loc. cit.*). Also like rubber squalene readily undergoes cyclization without rupture of the molecule, on treatment with acids.

It will be assumed that the polymerization of isoprene to form rubber has a similar mechanism to that which has been formulated in outline for the polymerization of indene, and it will be considered whether it is possible on this assumption to derive a formula for rubber which is in accord with the experimental evidence available. There are, of course, a considerable number of schemes according to which the polymerization of isoprene may be represented on the principle that the polymerization depends on the chemical addition of successive molecules with wandering of hydrogen, but the choice among such schemes is limited by two main considerations, namely, (1) the scheme must be capable of leading to very high polymeric products, (2) the formulas of the products must be consistent with the fact that on ozonolysis rubber yields preponderantly laevulinic acid and aldehyde.

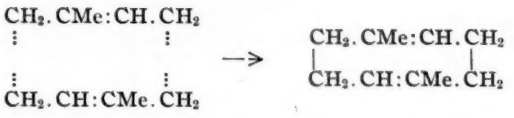
The first consideration rules out polymerization by what may be called mutual addition; for, if in the first polymeric stage two molecules of isoprene add on mutually, each to the other, the product is a cyclic one, and further polymerization within the conditions posited in the previous paragraph is not possible. Thus, for example, the mutual 1:4–1:2 addition of two molecules of isoprene may produce dipentene (A), or Lebedev's dimer, or Aschan's dimer, but further polymerization clearly could



(A)

not proceed along such lines. In point of fact, the substances just mentioned are all formed as oily by-products in the polymerization of isoprene to rubber.

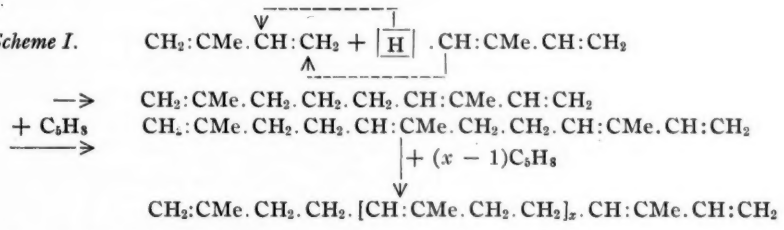
Similarly mutual 1:4–4:1 addition might conceivably give rise to the dimethylcyclooctadiene



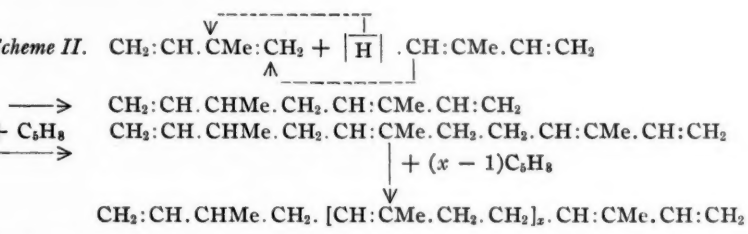
which Harries (*Ber.*, **38,** 1195 (1905)) originally regarded as the "chemical molecule" of rubber—a view which he later abandoned. But it could not, within the conditions, give rise to rubber.

The possible schemes for the polymerization of $(x + 2)$ molecules of isoprene conforming to the conditions are as follows. Two of these involve 1:2–; the others 1:4–addition. It will be remarked that there is present at each stage of the polymerization a conjugated system similar to that in the original isoprene, it being possible to regard all the products as isoprene with a single long-chain substituent.

1:2–Addition

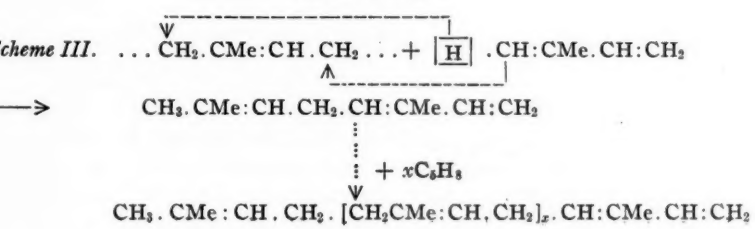


Products of ozonolysis:
($x + 1$) mols. laevulinic acid or aldehyde
2 mols. formic acid
1 mol. pyruvic acid or aldehyde.



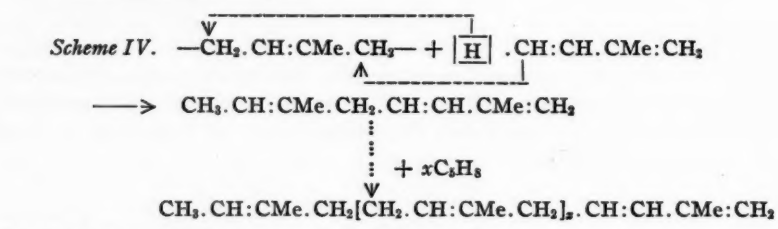
Products of ozonolysis:
x mols. laevulinic acid or aldehyde
2 mols. formic acid
1 mol. pyruvic acid or aldehyde
1 mol. pyrotartaric acid or aldehyde.

1:4– Addition



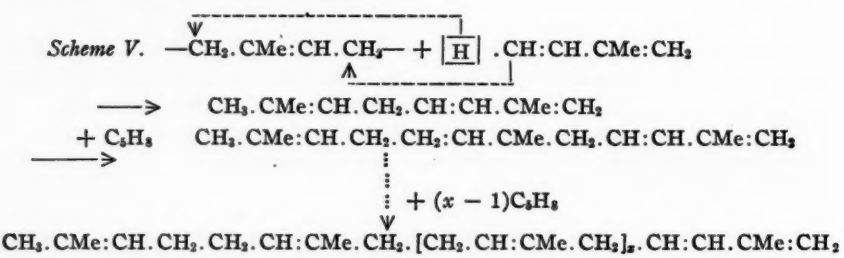
Products of ozonolysis:—
x mols. laevulinic acid or aldehyde
1 mol. formic acid
1 mol. pyruvic acid or aldehyde
1 mol. acetone
1 mol. malonic dialdehyde.

Scheme IV.



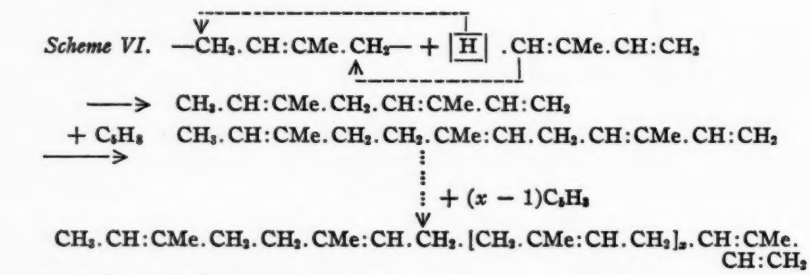
Products of ozonolysis:—
x mols. laevulinic acid or aldehyde
1 mol. formic acid
1 mol. pyruvic acid or aldehyde
1 mol. acetaldehyde or acetic acid
1 mol. acetoacetic acid or aldehyde.

Scheme V.



Products of ozonolysis:—
(x − 1) mols. laevulinic acid or aldehyde
1 mol. formic acid
1 mol. pyruvic acid or aldehyde
1 mol. succinic acid or aldehyde
1 mol. acetoacetic acid or aldehyde.

Scheme VI.



Products of ozonolysis:
(x − 1) mols. laevulinic acid or aldehyde
1 mol. formic acid
1 mol. pyruvic acid or aldehyde
1 mol. acetaldehyde or acetic acid
1 mol. acetonyl acetone
1 mol. malonicdialdehyde.

The formulation of rubber on lines such as those represented by the above schemes is not, the writer believes, incompatible with recorded data, *provided* the number of molecules of isoprene is very large, *i. e.*, provided that X in the above formulas is very large. It is true that measurements of the catalytic absorption of hydrogen by rubber (cf. Pummerer and Burkhard, *Ber.*, **55**, 3458 (1922)), of the addition of bromine, and of the molecular refraction (Macallum and Whitby, *Trans. Roy. Soc. Canada*, **18**, 191 (1924)) of rubber have always been considered as proving that rubber contains one double bond per isoprene unit, whereas each of the above formulas demands that if there are n units of isoprene in rubber the number of double bonds is $(n + 1)$. But if the molecule of rubber is very large, the measurements in question are not competent to distinguish between n and $(n + 1)$ double bonds; they could not, for example, distinguish between 1000 and 1001 double bonds per molecule.

The ozonolysis experiments which Harries conducted on rubber are not incompatible with the formulation of rubber on lines such as those proposed. Certainly those experiments demonstrated that the ozonolysis products are preponderantly laevulinic acid and aldehyde, but they were hardly of such a character as to enable it to be said that small proportions of other products, such as the above formulas would demand, do not occur. In the earliest ozonolysis experiments on rubber which Harries (*Ber.*, **37**, 1195 (1905)) conducted only 5 g. of ozonide were subjected to hydrolysis in each of two experiments, and in the second series of experiments (Harries and Hagedorn, *Ber.*, **45**, 936 (1912)) only 11.6 g. were hydrolyzed. And, though these experiments made it clear that the main products are laevulinic acid and aldehyde, the whole of the material was not quantitatively accounted for as these products: there was a certain amount of loss and of resin-formation. In a later experiment (*Untersuchungen über der natürlicher und künstlicher Kautschukarten*, Berlin, **1916**) carried out on a much larger quantity of ozonide, *viz.*, that derived from 300 g. of rubber, several significant facts emerged, *viz.*: (1) Small quantities of products were recognized which had not been observed in the earlier small-scale experiments. Formic acid (6.2 g.) and succinic acid (1.2 g.) were recognized, in addition to laevulinic acid and aldehyde. (2) The rubber employed was unextracted Para rubber. Now such rubber may, according to subsequent investigations (Whitby, Dolid, and Yorston, *J. Chem. Soc.*, **1926**, 1448; Whitby, *Trans. Inst. Rubber Ind.*, **1**, 12 (1925)), be assumed to contain at least 1 per cent of unsaturated fatty acids, mostly oleic, with some linoleic acid. Yet no ozonolysis products, such as azelaic acid or nonaldehyde, derived from this noticeable amount of unsaturated fatty acid were recognized in Harries' experiments. This suggests the conclusion that small amounts of ozonolysis products from the rubber hydrocarbon itself may also have been overlooked in the examination of the ozonide hydrolyzate.

If the number of molecules of isoprene taking part in the formation of rubber is of the order of, say, 1000, or even only 100, then the quantities of products other than laevulinic acid and aldehyde formed on ozonolysis would be very small and difficult to detect; and, as the above remarks on Harries' results suggest, the ozonolysis experiments of Harries cannot be considered as excluding the possibility of their occurrence. And, further, a number of the minor products of ozonolysis which the above formulas for rubber demand are such that, even in the ozonolysis of substances of known constitution which might be expected to yield them in considerable proportion, they are known to be difficult to identify after ozonolysis, presumably owing to their destruction during ozonolysis. This applies particularly to pyruvic aldehyde, malonic dialdehyde, and acetoacetic acid or aldehyde.

Of the six possible formulas for rubber which have been arrived at by the line of

argument followed above, it cannot, in the present state of our knowledge, be decided with certainty which is most likely actually to represent rubber. If the not unreasonable assumption is made that the addition of successive molecules of isoprene in order to build up a large polymeric molecule proceeds with the greatest regularity, then the choice in the case of 1:2-addition lies with Scheme I, and in the case of 1:4-addition with Schemes III or IV. Under these schemes, each successive addition takes place in the same sense as the preceding one, that is to say, for example, if (Scheme I) in the first step addition takes place to the vinyl group (—$CH{:}CH_2$), and not to the methyl-vinyl group (—$CMe{:}CH_2$), then in all subsequent steps addition to a vinyl group takes place.

On the other hand, the finding by Harries of succinic acid among the products of ozonolysis (*vide supra*) falls in with the formulation of rubber according to Scheme V.

The interesting studies of Lebedev and his co-workers on catalytic hydrogenation show that, when isoprene takes up one molecule of the symmetrical addendum, hydrogen, it takes it up simultaneously in all possible ways, *i. e.*, in the 1:2–, 3:4–, and 1:4– positions. Hence, it is not impossible that the addition of one molecule of isoprene to another such molecule may similarly proceed simultaneously according to all the three possible regular schemes, *viz.*, according to Scheme I, involving 1:2–addition and according to Schemes III and IV, involving 1:4– addition; and hence that rubber is a mixture of isomers. On the other hand, the asymmetry of isoprene, arising from the presence of a methyl substituent in the butadienoid system, may determine the addition in one direction only. Possibly measurements, now in progress in another laboratory (*Private communication* from E. H. Farmer), of the dipolar moment of alkyl-substituted butadienes will throw light on this matter.

One method by which it might be hoped to decide which scheme is followed in the polymerization of isoprene would be to isolate the early stages of polymerization, *e. g.*, the dimeric and trimeric stages, and determine their constitution. Ostromislenski (*J. Russ. Phys.-Chem. Soc.*, **47**, 1928, 1911 (1915)) claims to have obtained from isoprene, by heating it under certain specified conditions, an open-chain dimer, which he states is polymerizable to rubber; to which he gives the name β-myrcene, and for which is suggested the formula $CH_2{:}CMe.CH_2.CH_2.CH{:}CMe.CH{:}CH_2$. In careful repetitions of Ostromislenski's work, however, the writer, in conjunction with R. N. Crozier (*unpublished record*), has failed to secure from isoprene any β-myrcene: a compound which would be readily recognizable by its high refractive index.

In connection with the mode of approach suggested in the last paragraph, it is perhaps worth noting that ocimene, which probably has the formula $CH_2{:}CMe.CH_2.CH_2.CH{:}CMe.CH{:}CH_2$, and which therefore represents the dimeric stage in Scheme I, is not, so far as is known, accompanied by rubber in the plants in which it occurs. This consideration tells slightly against the formulation of rubber according to Scheme I, but cannot in the present state of our knowledge be regarded as very weighty.

Olivier (*Rec. trav. chim.*, **40**, 665 (1921); **44**, 229 (1925)), following a different line of argument from that pursued above, has already suggested the formulation of rubber in the way arrived at in Scheme I, but, as the foregoing discussion has indicated, there are five other similar possible formulas for rubber, which have substantially as good claims to consideration, and are in accord with our present condition of knowledge. It is not possible at present to decide with finality among these different but closely similar formulas.

An open-chain formula of a different kind has in recent years been advocated by

Staudinger, although the first suggestion of such a formula seems to have been made by Lebedev. This formula is as follows:

$$—CH_2.CH:CMe.CH_2.[CH_2.CH:CMe.CH_2.]_x.CH_2.CH=CMe.CH_2—$$

The formula involves the view that the molecule of rubber possesses free terminal valencies. Staudinger has endeavored to justify this conception by suggesting that the unsaturation, which might be expected to arise from such valencies, but which is not in fact observable, does not make itself evident because of the large size of the molecule.* The conception must, however, be declared to be so much out of harmony with accepted notions in organic chemistry that it cannot be accepted without further justification. It is true that the reactivity of a double bond may be greatly reduced by the circumstance that it occurs in a very large molecule, but free terminal valencies would differ in character from an ordinary double bond. If free terminal valencies appear in a given configuration of an open-chain molecule, it would not be expected that they would persist; it would be expected, rather, that the valencies in the chain would rearrange themselves, and that a double bond would appear in place of the free terminal valencies.

The conception of the polymerization of isoprene which Staudinger's formula for rubber would appear to imply is that the union of isoprene molecules involves what may be called mutual, partial 1:4-addition, at each stage of the polymerization process two molecules uniting mutually at one end only, while a free valency is left at the other end, there being no wandering of a hydrogen atom. As suggested in the previous paragraph, it would seem reasonable to suppose that, even if molecules of isoprene were at first to become united in this way, a rearrangement of valencies would occur, and that the terminal valencies would disappear.

Structure of Rubber

The idea that raw rubber consists of two parts, identical in proximate composition, but one soluble and the other insoluble, is a very old one. Weber (*J. Soc. Chem. Ind.*, **19**, 215 (1900)) states that he believes the idea to have been expressed first by Payen. It is referred to in the following terms by Engler and Herbst in an article published in 1887 (*Ladenburg's Handwörtbuch der Chemie*, **1887**, V, 479): "All these solvents [ether, chloroform, benzine, benzene, carbon disulphide, etc.] first swell the rubber greatly and then dissolve a part, while another part, ranging, according to the sort of rubber and the nature of the solvent, from 30 to 70 per cent of the original weight of the rubber, remains undissolved, even after several extractions. The undissolved part is tough, only slightly adhesive, only slightly elastic, colored, and of a reticular structure. The threads of the network swell on absorbing liquids, and contract again when the latter evaporate. The dissolved part, after volatilization of the solvent, is represented by a mass possessing little toughness and elasticity. Hence, in rubber two isomers are combined." Gladstone and Hibbert (*J. Chem. Soc.*, **53**, 679 (1888)) say: "It is well known that part of the rubber is soluble in benzene and other solvents, and that a part is insoluble." By applying chloroform to a sample of Para rubber, they found the insoluble residue to amount to 4 per cent only. They endeavored without success to separate "the two modifications" by partial precipitation with alcohol of a chloroform solution of rubber. Weber (*loc. cit.*) in a later experiment found 6.5 per cent of the specimen of rubber

* Cf., *e. g.*, the following: "Nach der . . . Auffassung (Staudinger, *Berichte*, **53**, 1082 (1920)), die von dem einen von uns geäussert wurde, reihen sich bei Polymerisationsvorgängen, die zu Kolloidmolekuln führen, die ungesättigten molekuln gleichartig in so langen ketten aneinander, dass die ungesättigte Natur der Endgleider—resp. der ganzen Molekul—gegenüber seiner Grösse nicht mehr hervortritt." (Staudinger and Fritschi, *Helv. Chim. Acta.*, **5**, 787 (1922)).

with which he was working to be insoluble in chloroform. He noticed that the content of carbon and hydrogen in the insoluble part did not agree with $(C_5H_8)_n$—a fact which was subsequently shown by Spence (*Quart. J. Inst. Comml. Res. Tropics*, Liverpool, **1907**) to be due to the presence of protein in the insoluble portion.

Caspari (*J. Soc. Chem. Ind.*, **32**, 1041 (1913)) applied petroleum ether for the separation of rubber into soluble and insoluble portions. The insoluble portion he referred to as the "pectous" form of rubber. He believed that it was possible to make a definite separation of rubber into two forms, soluble and pectous, and that the proportion of these, which varied from sample to sample, could be determined quantitatively. Stevens (*J. Soc. Chem. Ind.*, **38**, 194T (1919)) reported, however, that, on repeating Caspari's experiments, he had been unable to obtain concordant results in repeat extractions. "The proportion of soluble to 'pectous' appeared to depend on the period of extraction." "Moreover," he said, "I find that the 'pectous fraction,' if allowed to stand sufficiently long in cold petroleum spirit, dissolved wholly with the exception of a small quantity of slimy nitrogenous matter which settled to the bottom of the containing vessel."

In recent years, despite Stevens' findings, Caspari's views concerning the two-fold nature of rubber have been revived; originally by Feuchter, who applied ethyl ether instead of petroleum ether for the separation of the two parts (*Kolloidchem. Beihefte*, **20**, 434 (1925)). The portion of raw rubber which diffuses into ether when the rubber is allowed to stand in that liquid, and which corresponds to Caspari's "soluble" rubber, Feuchter designated Diffusion- or D-rubber, while the portion which remains, and which corresponds to Caspari's "pectous" rubber, he designated as the gel-skeleton. These two parts are now commonly known as sol- and gel-rubber, respectively, though Hauser (*Ind. Eng. Chem.*, **21**, 249 (1929)) prefers the designations α- and β-rubber. According to present usage, sol-rubber is such portion of raw rubber as diffuses from the swollen mass into the solvent when the rubber is allowed to stand in ethyl ether, whereas gel-rubber is such portion as remains behind.

The view that rubber consists of two parts sharply separable by means of ether has assumed great prominence in recent years. Several writers, among whom Hauser and Mark (*Kolloidchem. Beihefte*, **22**, 63 (1926); Ambronn Festschrift, **1926**, 64; *Gummi-Zeitung*, **40**, 2090 (1926); *Kautschuk*, **1925**, 10; Hauser, *Ind. Eng. Chem.*, **18**, 1146 (1926); **19**, 169 (1927); *Trans. Inst. Rubber Ind.*, **1926**, 239; *Ind. Eng. Chem.*, **21**, 249 (1929); etc.), are most prominent, have seen in the presence of sol and gel portions in rubber an explanation of the x-ray diffraction phenomena which rubber displays on stretching. It has also been called upon to explain the behavior of rubber on mastication (cf. *e. g.*, Hauser, *Kolloid-Z.*, Spec. No., April, **1925**; *India Rubber J.*, **69**, 663, 693 (1925); Park, *Ind. Eng. Chem.*, **17**, 160 (1925)), the Joule effect (cf. *e. g.*, Freundlich and Hauser, *Kolloid-Z.*, Zsigmondy Festschrift, **1925**, 15; Hauser and Mark, *Kolloidchem. Beihefte*, **23**, 64 (1926)), and the elastic behavior of rubber generally. Bruson, Sebrell, and Calvert (*Ind. Eng. Chem.*, **19**, 1033 (1927)) found the action of stannic chloride on rubber to yield a powder, part of which was soluble and part insoluble, and that the proportions of the two parts was identical with the proportions of "sol" and "gel" in the original rubber. As, however, the solvent used for the separation of the product of the action of the halide was benzene, while that used for the separation of the original rubber into "sol" and "gel" was ether, the coincidence of the proportions was probably fortuitous.

Freundlich and Hauser (*Kolloid-Z.*, Zsigmondy Festschrift, **1925**, 15) concluded from a microscopical study of the globules of *Hevea* latex that the globules consisted

of rubber in two distinct forms, and were composed of "a viscous liquid surrounded by an elastic shell" (Hauser, *Trans. Inst. Rubber Ind.*, **1926**, 239). The inner portion of the globules was considered as being rubber in a lower state of polymerization and the outer portion as rubber in a higher state of polymerization. These authors were apparently inclined at first to identify the two forms of rubber which they believed to be recognizable in the globules with the parts, sol and gel, obtainable from raw rubber by the ether diffusion process (*loc. cit.;* cf. Hauser, *Ind. Eng. Chem.*, **18**, 1146 (1926); *Trans. Inst. Rubber Ind.*, **1926**, 239), but more recently Hauser has apparently modified this opinion (*Ind. Eng. Chem.*, **21**, 249 (1929), footnote; cf. Hauser and Mark, *Kolloidchem. Beihefte*, **23**, 73 (1926)).

Von Weimarn (*Bull. Chem. Soc. Japan*, **3**, 157 (1928)) has concluded that the microscopical phenomena presented by rubber latex cannot be interpreted as proving the presence of a solid shell of rubber on the outside of the globules.

In an extensive series of measurements on the swelling of rubber which the writer started in 1923, it was early observed that when weighed pieces of smoked sheet were placed in organic liquids and the imbibition followed by weighing the pieces at intervals, in a large number of cases the weight at first rose and later fell. The fall was due to diffusion of part of the rubber from the swollen mass into the liquid, as could easily be shown by adding alcohol to the latter, when the diffused rubber was thrown out. The process of diffusion of rubber from the swollen gel went on gradually over a long period and did not apparently ever come to a sharp end. Some of the samples were kept under observation for four years, and in many such cases the whole of the rubber with the exception of the protein ultimately became dispersed in the liquid. Even in relatively poor swelling agents (see, *e. g.*, *o*-tolualdehyde, octylene, isoamyl oxalate, chloracetal, cyclohexanone in Table I), the dispersion process was often observed to have completed itself after 3–4 years. The general impression made by the mass of data which has been secured on the swelling of raw rubber is that in general the process of diffusion never comes to a definite end or allows of a sharp separation of the rubber into a "sol" and a "gel" portion. A little of the data is quoted in Table I.

TABLE I

IMBIBITION OF ORGANIC LIQUIDS BY SMOKED SHEET (ORIGINAL WEIGHT : 1)

Liquid	Weight after Periods of Days						
	1	2	3	7	31	62	4 Years
Octylene	6.68	4.46	4.22	3.31	..	..	Completely dispersed.
o-Tolualdehyde	3.67	4.66	4.88	4.00	1.65	..	
Chloracetal	5.99	5.57	4.71	2.50	1.18	..	
Cyclohexanone	6.14	4.84	2.83	1.40	..	..	
n-Valeric anhydride	1.84	2.44	2.95	3.39	..	..	
Isoamyl oxalate	1.51	2.13	2.76	3.40	..	..	
Ethyl-*m*-toluate	7.98	8.39	8.25	6.07	2.92	2.36	
Isobutyl acetate	9.00	8.90	6.96	3.10	1.61	..	
p-Tolualdehyde	2.83	3.59	4.15	4.24	2.41	0.87	
o-Tolunitrile	5.67	7.10	7.79	7.43	4.82	2.43	
n-Propyl ether	5.98	5.25	4.29	3.03	2.27	1.87	
Safrole	9.51	11.60	12.01	10.36	5.86	4.51	
p-Cresyl ethyl ether	13.18	14.85	13.16	9.02	5.66	4.81	
Butyrophenone	4.83	5.95	6.18	4.30	..	1.60	
Allyl isothiocyanate	7.44	9.60	9.65	5.63	2.82	..	
Lauryl chloride	7.49	8.52	7.86	5.76	3.02	..	
Phenyl ethyl bromide	7.23	9.03	9.26	5.36	2.91	..	
Nonylic acid	3.37	5.00	6.50	6.91	1.58	..	
Tripropylamine	9.50	7.02	5.45	4.09	2.85	2.12	

The examples quoted in Table I have been chosen to represent liquids belonging to a considerable number of different chemical types. The figures show the weight of the swollen mass after various periods of time, the initial weight being taken as 1. In some, but not all cases, the samples were examined after a lapse of four years. Most of the liquids are not among the most powerful swelling agents. With such powerful swelling agents the swollen mass is usually too weak to handle for the purpose of weighing after one day. It may be mentioned for purposes of comparison that the weight of, *e. g.*, benzene imbibed in one day by the specimen of rubber in question was 24.22 parts; of ether, 11.10 parts.

If the point at which the process of diffusion becomes very slow were to be taken as the end point, the proportions of "sol" and "gel" which it would be concluded that the rubber contained would undoubtedly vary greatly with the solvent used.

Though there is no sharp end to the diffusion process, the ease with which diffusion occurs and the proportion which will diffuse into the solvent with reasonable rapidity, vary in different liquids, and are apparently influenced by (*a*) the swelling power of the liquid, (*b*) its viscosity. Even in a given liquid the proportion of rubber which will diffuse in a reasonable time from a given sample of rubber can be greatly modified. Such modification can be brought about by (among various means) adding small quantities of certain agents, especially strong organic bases and acids, which increase the amount of the liquid inbibed by the rubber. When studying the electro-viscous effect in rubber sols in 1924, the author employed diffusion into ether and petroleum ether for the purpose of securing rubber free from protein and observed that the addition of small amounts of piperidine, diethylamine, sodium ethoxide, and ammonia greatly increased the proportion of diffused rubber obtained from a given sample of raw rubber. Previously it had been found that small amounts of piperidine increased the swelling of vulcanized rubber in benzene (Whitby and Jane, *Colloid Symposium Monograph*, **1924**, II, 16).

The influence of bases on the swelling and dispersion of raw rubber may be illustrated by the following data:

SMOKED SHEET IN PETROLEUM ETHER (B. P. 25°–45°)

A

	Petroleum Ether Alone	Petroleum Ether Containing 5 Drops Piperidine per 10 Cc.
Weight originally	0.1317 g.	0.1075 g.
Weight after swelling 24 hours	1.0925 g.	1.7435 g.
Increase in weight	735 per cent	1520 per cent

B

	50 Cc. Petr. Ether	40 Cc. Petr. Ether + 10 Cc. Ethereal Solution NH_3
Weight originally	0.60 g.	0.60 g.
Weight of diffused rubber pptable. after 8 days' standing	0.05 g.	0.31 g.

In a good swelling agent such as benzene, the proportion which will readily diffuse from a sample of smoked sheet is greater than in a poorer swelling agent such as ether or especially petroleum ether. Thus, for example, in an experiment in which 3.83 g. of smoked sheet was left in 190 cc. of benzene with occasional very gentle agitation, 75.5 per cent of the rubber has dispersed in 7 days.*

A study of the behavior of vulcanized rubber in swelling agents also fails to afford any evidence of the presence of two sharply distinct parts. In current writings on

* When 0.3 g. of the diffused rubber was carefully tested for nitrogen with the aid of metallic potassium, a completely negative result was obtained. The volume of the swollen, undispersed nitrogen-rich residue in this experiment was about 42 cc.

the structure of rubber less attention has been given to vulcanized than to raw rubber, though the elastic properties which any theory of the structure of rubber must ultimately endeavor to explain are exhibited in much greater perfection by the vulcanized than by raw material. If, however, the x-ray diffraction phenomena shown by raw rubber are ascribed, as they currently are, to its two-fold (sol-gel) nature, then it is natural to assume that, since vulcanized rubber shows similar x-ray phenomena, it too consists of two parts, though the proportion in which the two parts occur may be regarded as different, owing to the conversion during vulcanization of a portion of the sol into the gel form. (Cf. Hauser, *Trans. Inst. Rubber Ind.*, **1926**, 243: "During vulcanization the liquid rubber phase is more or less gelled or polymerized.")

Observations on the behavior of vulcanized rubber in swelling media show, as in the case of raw rubber, no evidence of the presence of two clearly distinct parts. It is usually said that vulcanized, in contradistinction to raw rubber, is insoluble in all liquids. The writer has, however, found that, by leaving fully vulcanized rubber in swelling agents for periods up to four years in the dark, the rubber gradually dispersed in many cases. Further, the rubber dispersed completely or substantially so, and there was no indication of the presence of a soluble and an insoluble phase. Examples of liquids in which vulcanized rubber was observed to disperse completely in the course of time are ethyl benzoate, butyl acetate, butyl oxalate, ethylene glycol dipropionate and twenty-one other esters; methyl iodide, bromoform, isobutyl chloride, *o*-chlorotoluene, and twelve other halogenated hydrocarbons; benzene, valeric acid, ethyl propyl ketone, cyclohexanone, butyl isothiocyanate, hexyl alcohol, and *o*-tolualdehyde, diisobutylamine, *n*-propyl ether.

Considerations such as those just put forward concerning the behavior of rubber in swelling agents serve to indicate the inadequacy of the view that rubber consists of two parts—a sol or liquid phase and a gel or solid phase. In order to arrive at more positive conclusions regarding the structure of rubber, it now seems desirable to consider some facts about certain artificial polymers, especially about certain elastic ones. There is now known a number of artificial polymeric products which exhibit elastic properties either at ordinary or at elevated temperatures. Examples of such products are as follows: synthetic rubbers from conjugated dienes of low molecular weights, polymers from methyl acrylate and similar esters, polystyrene (metastyrene), polyvinyl acetate, polyethyl itaconate, rubber hydrochloride (Whitby and Jane, *Trans. Roy. Soc. Canada*, **20**, 130 (1926)), the reaction product from isoprene and sulfur dioxide (Ostromislenski, *J. Russ. Phys. Chem. Soc.*, **1915**). The first two of these materials are elastic at room temperature; the others, when warmed or swollen. Of these materials polystyrene and polyvinyl acetate have been most closely investigated.

Polystyrene at ordinary temperatures is a hard solid. In massive pieces or films, it is clear; as precipitated, white. At ordinary temperature it is not elastic, the films being brittle and the powder friable, but when warmed or swollen it shows elastic properties essentially similar in kind to those of raw rubber. The temperature—the "elasticity temperature"—at which autopolymerized styrene is elastic in the absence of a swelling agent is about 65°. The general similarity of the behavior of polystyrene to that of raw rubber is demonstrated by such facts as the following:

(*a*) Both polystyrene and rubber have an "elasticity temperature" below which the material becomes inextensible or "frozen." For rubber, however, this temperature is somewhat below ordinary room temperature.

(*b*) Polystyrene shows the effect known in rubber as "racking"; that is to say,

if stretched while above its elasticity temperature and then, while extended, cooled below that temperature, it retains the extension, and, if then heated above its elasticity temperature, retracts. (This phenomenon can readily be observed in raw rubber by stretching a strip of smoked sheet and then, while maintaining the extension, cooling it in a stream of cold water. The rubber will be found to retain its extension if now released, but when warmed slightly, as, for instance, by holding it in the palm of the hand, will undergo retraction. It should be mentioned that the term "racking" is not very clearly defined and has sometimes been used to denote particularly the extension of rubber at elevated temperatures to lengths greatly exceeding those to which it can be extended without rupture at ordinary temperature.

In this usage of the term too, polystyrene can be "racked," *i. e.*, at temperatures well above the elasticity temperature it can be extended to lengths much beyond those at which near the elasticity temperature it suffers rupture.)

(*c*) Like rubber, polystyrene shows elastic after-effect, *i. e.*, on releasing a specimen which has been stretched, a slow retraction follows on the initial rapid retraction. This is shown by the following experiment. A strip 6 cm. long was placed in water at 95°, stretched to a length of 22.5 cm., and then released under no load. The Table below gives the length of the strip at intervals after its release.

TABLE II

REACTION OF POLYSTYRENE

Time after release (sec.).....	0	1	7	102	310	900
Length (cm.).....	22.5	10	9	8	7.5	7

(*d*) When the material is stretched and then released, the amount of set left after any time is profoundly influenced by the length of time for which the material has been maintained in a stretched condition. In an experiment, strips of polystyrene were stretched 450 per cent at 95°, and after being held at this extension for various periods of time, were released. The retraction over a period of time was followed. The data in Table III indicate the character of the results obtained.

TABLE III

INFLUENCE OF PERIOD OF STRETCHING ON RETRACTION OF POLYSTYRENE

Time kept at 450% (min.).....	0	5	10	90
Extension immediate after release, per cent.....	50	150	175	300
Extension 200 sec. after release, per cent.....	0	55	75	150

The following experiment carried out with strips of raw rubber (smoked sheet) shows that the set in rubber is similarly influenced by the length of the period of time for which the material is maintained in a stretched condition. Strips were held at an elongation of 200 per cent at 48° for various periods of time, and, after being released, they were allowed to stand at room temperature for ten days, when

TABLE IV

SET IN RAW RUBBER AFTER EXTENSION FOR VARIOUS TIMES

Time Kept at 200% at 48° (Min.)	Set at Room Temperature, $\frac{\%}{E_1}$	Set at 100° $\frac{\%}{E_1}$
5	22.5	17.5
10	27.5	17.5
15	37.5	20
30	40	27.5
60	52.5	35
120	62.5	42.5
240	67.5	47.5

no further retraction could be observed. The set remaining is tabulated as E_1. The strips were then heated for one hour at 100°, and, after they had been allowed to cool to room temperature, the set (E_2) was again measured. The results are given in Table IV.

(*e*) The higher the temperature at which either rubber or polystyrene is stretched to a given extent, the greater is the set remaining on release. This was observed qualitatively for polystyrene. For raw rubber more exact data were secured. Strips of smoked sheet were held at different temperatures for 30 minutes at an extension of 200 per cent, and were then allowed to retract at room temperature for 10 days (set: E_1) and subsequently were heated to 100° and the set (E_2) again measured. Table V gives the results.

TABLE V

INFLUENCE OF TEMPERATURE OF STRETCHING ON SET IN RAW RUBBER

Temperature during Extension	Set at Room Temperature, % E_1	Set at 100°, % E_2
20°	17.5	15
25	22.5	15
35	30	20
40	47.5	22.5
60	55	45
70	70	55
83	90	75

(*f*) Both with polystyrene and with rubber, the greater the length to which a specimen is extended, the greater is the set present under given conditions. This was determined only qualitatively for polystyrene. For rubber (smoked sheet) the following more exact data were secured.

TABLE VI

EFFECT OF ORIGINAL ELONGATION ON SET IN RAW RUBBER

Elongation Maintained for 30 Minutes at 48°, %	Set after 10 Days at Room Temperature, % E_1	Set at 100°, % E_2
50	7.5	7.5
100	20	17.5
150	27.5	20
200	40	27.5
250	55	30
350	125	52.5
400	142.5	..

The data given in the last three sections show that, both for raw rubber and polystyrene, the longer the material is kept stretched, the higher the temperature at which it is stretched, and the greater the extent to which it is stretched, the greater is the set. Such increase in set represents the transformation of elastic into irreversible deformation: it connotes a loss of elastic properties. A better understanding than we can now claim to possess of what is taking place during such transformation will be necessary before we can arrive at a fully satisfactory picture of the intimate structure of the elastic materials in question.

(*g*) The following experiment was carried out on a strip of polystyrene of cross section 2.05 sq. mm. A constant load of 75 g. was maintained throughout; the temperature was first raised at a definite rate; then lowered; again raised, and so on. The elongation at the end of each period of heating and cooling and at certain intermediate points is shown in the following table.

TABLE VII

HEATING AND COOLING POLYSTYRENE UNDER FIXED LOAD

	Temperature Rising	Temperature Falling	Elongation, %	
1.	55°		0	
	65		10.8	
	75		35.2	
	80		457	
		1a. 70°		473
		64		481
		40		481
2.	67		481	
	70		495	
	79		523	
		2a. 74		528
		70		528
3.	79		560	
		3a. 25		560
4.	79		590	

These results indicate a behavior analogous to that of rubber in two respects. (*a*) During the first period of cooling, it will be noticed, "creep" takes place until the temperature has fallen below the elasticity temperature. (*b*) During the periods, 1, 2, 3, 4, the final extension increases in each succeeding period, but the difference between the extension at the end of the first and of the second period is greater than the difference between that at the end of any other two successive periods. This clearly recalls the behavior of rubber when subjected to successive cycles of extension and retraction. With rubber, the difference between the first and the second cycles is greater than that between any other two successive cycles (see Whitby, *Plantation Rubber and the Testing of Rubber*, **1920,** Chap. XVIII).

(*h*) It has been shown by Rosbaud and Schmid (*Z. tech. Physik*, **9,** 98 (1928)) that even extremely small loads will cause raw rubber to extend, and will even rupture it if allowed to act for sufficiently long periods. A similar behavior was observed with polystyrene. For example, while a load of 45 g. applied at 95° to a strip 2.13 sq. mm. in cross section caused relatively rapid stretching and produced an elongation of 122 per cent in 5 seconds, even a load of 5 g. would produce the same elongation if allowed to act for 225 seconds.

(*i*) Sols of autopolymerized styrene show many similarities to sols of rubber. At the same temperature and in the same solvent sols of rubber and of polystyrene have similar viscosities. The nature of the solvent affects the viscosity of sols of the two materials in, broadly, a similar way. The lowest viscosities in both cases were observed in the same solvent, *viz.*, acetal.

Another elastic polymer on the elastic properties of which some measurements have been made is polyvinyl acetate (Whitby, McNally, and Gallay, *Trans. Roy. Soc. Can.*, **1928,** Pt. III, 27). This material has a lower elasticity temperature than autopolymerized styrene (it becomes readily extensible at a temperature of 40°), and its elastic properties are poorer than those of the latter. A strip of cross section 5.6 sq. mm. was subjected to a load of 75 g. and the temperature was raised

TABLE VIII

EXTENSION OF POLYVINYL ACETATE WITH RISING TEMPERATURE

Temp., ° C.	15	19	22	27	31	34	35	36	37	37.5
Elongation, %	0	3	12.5	25	40	56	72	87	103	119

Temperature	38	38.3	38.5	39.2	40.0	40.2	40.6	41.0	41.5
Elongation	134	150	181	212	275	368	466	525	710

over a period of 30 minutes from 15° to 41.5°. Table VIII shows the extension observed at various temperatures. On releasing the strip at 41.5°, it retracted to an elongation of 103 per cent in 10 minutes. Polyvinyl acetate can be extended to very great lengths, but after such extension its recovery is, as in the case of raw rubber similarly extended, less complete than after moderate extensions. Thus, a specimen stretched at 50° to 2710 per cent elongation, when allowed to retract under no load, still had an elongation of 300 per cent after 10 minutes.

The data for polystyrene given above refer to styrene which had been allowed to polymerize spontaneously at room temperature. This material has so high a molecular weight that it produced no appreciable depression of the freezing point of benzene. Polystyrene prepared by heating styrene has on the other hand a lower and measurable molecular weight, and possesses a lower elasticity temperature and poorer elastic properties. A sample prepared by heating styrene for 48 hours under reflux at 140° had a molecular weight, determined cryoscopically, of 1920; and one prepared by heating styrene for 24 hours in a closed vessel at 180°, a molecular weight of 2180. These samples became soft at 40° and readily extensible at 47°. While they could be extended readily, their power of retracting was poor. At 72° a specimen extended 800 per cent and then released, retracted to 600 per cent and remained there. A specimen extended to 1400 per cent at 89° and then released, retracted only to 1100 per cent and remained there.

Polystyrene can be rendered elastic, not only by raising it to its elasticity temperature, but also by introducing a swelling agent, when it becomes elastic at room temperature. Further, recovery from deformation was found to be more nearly perfect in such swollen polystyrene than in polystyrene rendered elastic by heating. Thus, *e. g.*, a gel of autopolymerized styrene containing 50 per cent of ethyl oleate, when stretched 1300 per cent, showed practically no set within a few minutes of its release. If autopolymerized styrene is precipitated from a solution, the fresh precipitate is strikingly elastic and reminiscent of raw rubber; it is in fact more extensible than raw rubber, and it recovers from extension with a "snap."

If such precipitated polystyrene is allowed to stand in the air, it gradually loses its extensibility as the solvent evaporates and finally becomes friable. That is to say, while in a swollen condition, it is elastic at room temperature; when unswollen, inelastic. A permanently elastic material can be obtained by incorporating with polystyrene a non-volatile swelling agent, such as tricresyl phosphate or isoamyl phthalate.

Having thus reviewed the behavior of two typical elastic colloids which are generally similar in properties to raw rubber, it is now desirable to consider whether any of the facts about the structure of these materials throw light on the question of the nature of rubber and current views concerning its structure. In the first place, it may be noted that, since at no stage in their preparation are polystyrene and polyvinyl acetate in the form of an emulsion or suspension, and since nevertheless they exhibit elastic properties similar to those of raw rubber, the peculiar character of the globules in rubber latex, if such exists, is not essential to the occurrence of elasticity in organic colloids and is probably of no significance in the explanation of the elastic behavior of rubber.

In the second place, it is to be noted that neither polystyrene nor polyvinyl acetate consists of two parts only—a "sol" and a "gel" form—but that both materials are more highly heterogeneous. In their heterogeneity these materials resemble other non-elastic polymers. The high degree of heterogeneity in non-elastic highly polymeric products is well shown by results obtained with polyindene. A sample

of this product, prepared by the action of stannic chloride on indene was separated by fractional precipitation into the following fractions (Whitby and Katz, *J. Am. Chem. Soc.*, **50**, 1160 (1928)).

TABLE IX

HETEROGENEITY OF POLYINDENE

No. of fraction	1	2	3	4	5	6	7
M. p.	261–5°	247–50	236–41	231–5	219–23	198–201	164–7
Mol. wt.	3320	2785	2560	2295	1990	1568	952

Further fractionation showed, as was to be expected, that the above fractions were themselves heterogeneous.

A similar state of heterogeneity was found to exist in the elastic polymeric product, polyvinyl acetate (Whitby, McNally, and Gallay, *loc. cit.*). A sample of this material which at room temperature was hard was placed in acetone. It swelled, and then on standing the material gradually diffused into the free liquid. After a certain amount had passed into solution, the liquid was poured off, and fresh acetone added. A second fraction was thus obtained. This was repeated until four fractions had been obtained and the whole of the colloid had dispersed. The four fractions of polymer were thrown out by the addition of water and dried. As the results in the following table show, the fractions differed markedly in molecular weight and in the viscosity of their sols.

TABLE X

FRACTIONATION OF POLYVINYL ACETATE

No. of Fraction	Mol. Wt. (Cryoscopically in Benzene)	Relative Viscosity of Sol (0.328 G. in 100 Cc. Benzene). (Benzene = 1)
1	566	1.303
2	1281	2.725
3	3483	5.878
4	6192	8.389

Undoubtedly further fractionation would have shown each of the above four fractions to be resolvable into sub-fractions of different molecular weight and properties.

Polystyrene also was found to be heterogeneous. In the case of the polymers already mentioned as being produced by heating styrene, heterogeneity was easily recognizable by treating the materials with ether, acetone, orethyl oxalate. When the much more highly polymerized product obtained by allowing styrene to undergo autopolymerization is treated with ether or acetone, no solution or apparent swelling takes place, and when treated with diethyl oxalate, only a very slight swelling. When, however, styrene polymerized by heating at 140° or 180° is treated with these liquids, the major part rapidly goes into solution, but there remains a portion which fails to disperse and which on standing settles out as a white powder. This is clearly a fraction of the material more highly polymerized than the rest. If it is separated and treated with benzene (a solvent for highly polymerized styrene), it readily goes into solution.

The heterogeneity of autopolymerized styrene was demonstrated both by fractional precipitation and fractional diffusion. To 1.5 g. dissolved in 100 cc. benzene was added 42.8 cc. alcohol, and the precipitate separated; 0.45 cc. more alcohol was then added, and then a further quantity of 5.5 cc., the precipitate being separated after each addition. When these fractions were made up in benzene to sols containing 0.328 g. per 100 cc. benzene, they showed the following viscosities:

TABLE XI

	Relative Viscosity of Fractions of Polystyrene
No. 1	5.40
No. 2	5.29
No. 3	2.31

A sample weighing 2.17 g. was placed in a bottle with 100 cc. benzene, and, after a part had diffused into the liquid, 50 cc. was poured off and fresh benzene added. Three fractions were collected. After precipitation with alcohol, drying, and solution in benzene (0.328 g. per 100 cc. benzene), the sols showed the following viscosities.

TABLE XII

FRACTIONS OF POLYSTYRENE BY DIFFUSION

No. of Fraction	Weight	Relative Viscosity of Sol
1	0.42 g.	4.90
2	0.74 g.	5.07
3	0.56 g.	5.27

A sample of synthetic methylrubber, prepared by the thermo-polymerization of dimethylbutadiene, was also found to be resolvable into fractions having different properties, as the following data will show:

TABLE XIII

FRACTIONATION OF METHYLRUBBER

Fraction no.	1	2	3
Time of flow of sol (0.854 g. in 20 cc. benzene) (sec.)	55.4	67.8	81.3

In the author's view, the heterogeneity of rubber is similar to that of the polymeric products just discussed; that is to say, rubber consists, not merely of two parts, but is a mixture of an unbroken series of polymers representing a rather wide range of degrees of polymerization. This view of the structure of rubber is in accord with the behavior of rubber in swelling agents. The ease of dispersion of a lyophilic polymer of a given molecular magnitude varies in different liquids. Hence the proportion of a given sample of rubber which will diffuse readily, *i. e.*, the proportion of "sol" rubber obtained, will differ in different liquids. In a given liquid, the ease of dispersion varies with the molecular magnitude of the polymer, the higher the degree of polymerization, the less rapid being the dispersion. Hence the rate with which dispersion of a sample of rubber will take place will diminish as the proportion which has undergone dispersion increases. But even the highest polymers present will in many solvents disperse if given time, and hence it is found, as already stated, that the whole of the rubber disperses in many cases if left to stand for a long time.

The difficulty with which the later fractions in rubber undergo dispersion is due primarily to the fact that they represent the highest polymeric stages present in the rubber. Though the presence of a protein network may possibly retard the diffusion process somewhat, it is not, the author believes, the main cause of the slowness with which the higher fractions of rubber disperse. Observations on the dispersion of vulcanized oils indicated clearly that, even in the complete absence of a protein network, dispersion became slower and slower as the degree of polymerization increased. It was observed that after the polymerization of a sulfurized oil (containing no free sulfur) had proceeded just to the point at which the material had set solid, the product dispersed readily in benzene, but that as polymerization was carried further by continued heating, dispersion became slower and slower and that finally a product was obtained which, like vulcanized rubber, dispersed in

benzene only after standing for several years. As further showing that a high degree of polymerization, apart from the presence of a protein network, is sufficient to produce slowness of dispersion, it may be noted that diffused rubber (obtained by means of petroleum ether) after being vulcanized behaves in solvents in a manner essentially similar to that of vulcanized rubber containing protein. It may also be noted that, as already mentioned, autopolymerized styrene disperses far less readily than the less highly polymerized thermopolymerized styrene.

A striking case of the difficulty of dispersion due apparently to the high degree of polymerization in the material is presented by polymethyl acrylate. This material, which was prepared by heating methyl acrylate for half an hour on the water-bath with 0.1 per cent benzoyl peroxide, has a molecular weight so high that no appreciable depression of the freezing point of benzene is observable. It showed a higher degree of swelling than any other polymeric product encountered, taking up,

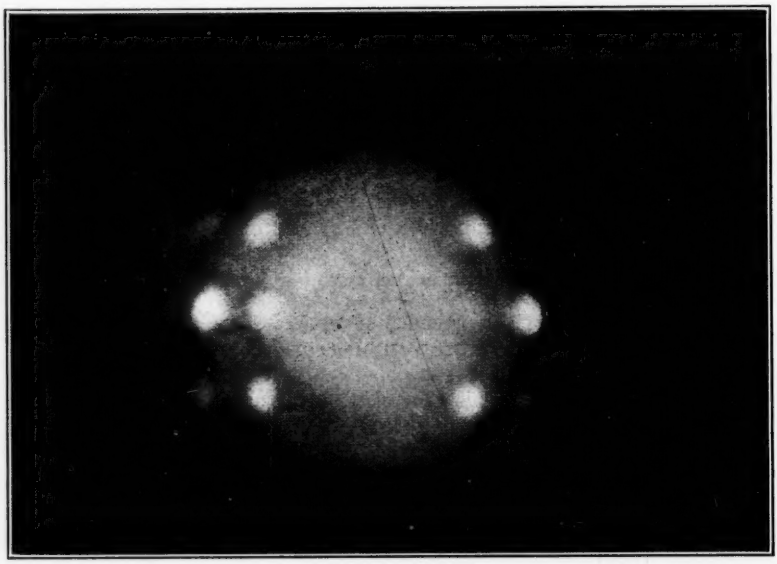


Figure 1—X-ray pattern from diffused rubber stretched 1800 per cent

e. g., 88.8 times its weight of methyl acetate, yet failed to disperse in a reasonable time even in good swelling agents.

Direct experimental evidence of the heterogeneity of raw rubber was obtained by carrying out the diffusion process fractionally, fractions being poured off and fresh liquid added from time to time. The viscosity of the sols (adjusted to the same rubber-content) was compared and found to differ widely. Diffusion rubber was also separated by fractional precipitation into fractions having different properties. The data obtained in this connection will be published elsewhere. They afford conclusive evidence that diffusion-rubber ("sol" rubber) is far from homogeneous.

It may be mentioned, further, that diffusion-rubber shows all the normal behavior of rubber. Naturally, its behavior is not quantitatively identical with that of the original rubber from which it is obtained, since, as it represents only a portion of the latter, the range of polymeric stages in it is not identical with the range in the origi-

nal rubber. It can, however, be vulcanized, especially if small proportions of fatty acid and accelerator are added; it shows "racking" phenomena; it gives an x-ray diffraction pattern when stretched; it requires breaking down on a mill in making up a stock, and the ease of breakdown is not strikingly different from that of the original rubber. Fig. 1 shows an x-ray diffraction pattern given by diffused rubber. This specimen was prepared by removal of resin by extraction with petroleum ether-acetone (30 : 70) at room temperature, followed by diffusion of a part of the rubber into benzene. The diagram was made after racking the rubber to an elongation of 1800 per cent. At 300 per cent extension a diagram was obtained, but was much less distinct.* If diffused-rubber ("sol" rubber) were, in fact, homogeneous, and if the occurrence of x-ray diffraction phenomena on stretching were in fact due to the presence of "sol" and "gel" phases, then diffusion-rubber would not be expected to show a diffraction pattern. That it does so is therefore significant.

There is no evidence of the presence in rubber of a liquid phase. When the diffusion of raw rubber was carried out fractionally, it was found that, even when the first fraction collected was very small and represented only about 5 per cent of the whole, the material was not a liquid but an elastic solid.

The physical properties of the polymeric products derivable from a given monomer depend on the average degree of polymerization and on the width of the range of polymeric stages present. This applies to the melting or softening point, the ease of cracking on pyrogenic decomposition, the viscosity of sols of a given concentration and the elasticity. As data given in Table X for polyvinyl acetate fractions indicate, there is in the case of lyophilic polymers a general parallelism between the degree of polymerization, as shown by the mean molecular weight, and the viscosity of sols of a given concentration; the higher the degree of polymerization, the greater being the viscosity. Now, rubber, as already mentioned, can be separated into fractions which give sols having different viscosities. The molecular weight of these fractions has not hitherto been satisfactorily determined, but it is fair to assume that the molecular weight of the fractions parallels their viscosity.

The elastic properties of polymeric products such as those under consideration are to be regarded as determined by the mean molecular weight and the range of molecular weights in the mixture. The dependence of elastic properties on the degree of polymerization is well shown by a comparison of auto- and thermo-polymerized styrene. Styrene polymerized by heating at 140° or 180° has a mean molecular weight of the order of 2000 and gives sols of low viscosity, whereas styrene allowed to polymerize spontaneously has a vastly higher molecular weight (probably of the order of 100,000 or higher) and gives sols of high viscosity. And, as already mentioned, the elastic properties of the former are very much inferior to those of the latter. Similarly, the synthetic rubber obtained by heating isoprene at 85° has a molecular weight of the order of 4000, gives sols of a much lower viscosity than those from natural rubber, and, correspondingly, has elastic properties much inferior to those of raw rubber.

For the polymeric products obtainable by a given method of polymerization from a given monomer there is probably a certain degree of polymerization which is optimal for the possession of good elastic properties. If the degree of polymerization is too low, the material, while readily deformable, shows poor recovery from deformation; if the degree of polymerization is too high, the deformability is small and the material is tough, brittle, or "short." In a certain intermediate state of

* The author is indebted to T. N. White, of the Physics Department, McGill University, for taking these diagrams. Kα rays from copper were used.

polymerization, the material is both deformable and retractable. As the case of polystyrene shows, the deformability may not be present at first, but may be brought into evidence only by altering the mechanical properties by swelling or heating the material.

It is very desirable that there should be made a closer analysis than is possible at the moment of the complicated phenomena presented by raw rubber and the artificial elastic colloids previously mentioned, all of which are much less perfectly elastic than properly vulcanized rubber. Such an analysis will call for the introduction of certain new terms. One such term which may be suggested is "elastic yield value." Heating or swelling polystyrene increases the deformability by reducing the yield value. Such deformability, however, being primarily elastic and not plastic, and the term "yield value" having been assigned to the deformation and flow of plastic materials, it would seem desirable in the case of elastic materials to refer to "elastic" yield value.

The phenomena presented by the imperfectly elastic materials cited is complicated by the fact that, as already pointed out, there may take place under suitable conditions a change from elastic to irreversible deformation, *i. e.*, plastic flow may follow the initial elastic deformation, and the material may acquire a "set." Further, as is shown by the data for the retraction of raw rubber given in Tables IV–VI, a part of the residual deformation which shows itself under certain conditions as "set" may not truly be due to plastic flow but may be present only because the "elastic yield value" is too high at room temperature and may disappear on raising the temperature. A phenomenon which is probably due similarly to a reduction in the elastic yield value as a result of increase of temperature is the retraction which follows the application of heat to a strip of rubber under load.*

The effect of swelling agents in reducing the elastic yield value, and thus in rendering elastic colloids which are not normally so, is not confined to the cases, such as polystyrene and polyvinyl acetate, which have already been mentioned. It is also observable with hydrophilic colloids such as the proteins, silk fibroin, and wool keratin. Von Weimarn records that when silk fibroin is dissolved in certain concentrated aqueous salt solutions and then precipitated by the addition of alcohol, it shows elastic properties when the degree of hydration is suitable. "As the degree of dehydration increases," he says, "we may witness the realization of every possible transition stage marking the gradual conversion from the condition of an extremely viscous syrup through a gluey mass to that of an elastic rubber-like jelly (in which condition an *elastic* extension to twice or even four times the former length is possible) and thence to that of masses possessing the consistency of an animal tendon, till it finally reaches the state of an altogether solid mass, so solid that when in thin sheets it may be broken."

Similarly, the elastic properties of wool are greatly influenced by the extent to which the protein is swollen by moisture in the fiber. (Cf. Shorter, *J. Textile Inst.*, **1924**; *Trans. Faraday Soc.*, **1924**; Speakman, *Trans. Faraday Soc.*, **25**, 388 (1929).) If a wool fiber containing the normal water content is stretched, and then while stretched is dried, it will be found to retain its extension on release, but will then retract if again allowed to absorb moisture, *i. e.*, if the elastic yield value of the protein is reduced by allowing it to swell somewhat. Advantage is taken of this phenomenon in the treatment of wool known as "crabbing."

Though wool is much less extensible than rubber, there is broadly an analogy, not only in this respect, but also in other respects between the elastic behavior of wool

* This phenomenon was designated by the lecturer some years ago as the Joule Effect. (See *Plantation Rubber and the Testing of Rubber*, **1920**, Chap. XX.) Since then the term "Joule Effect" has also been used to indicate the rise of temperature which occurs on stretching rubber.

and of raw rubber. In both cases time plays an important part in the result of any series of mechanical manipulations through which the material may be made to pass. Strictly speaking, there is no such thing in either case as a stress-strain diagram, but only a stress-strain-time diagram. This is perhaps more obvious with wool than with rubber. On loading a wool fiber, there occurs first a rapid extension, which is reversible, and this is followed by a further, slow extension, which is only partly reversible and is greatly influenced by the length of time over which the load acts, owing to plastic flow of the material.

The ultimate explanation of the fact of elasticity in certain organic colloids is not yet in sight. It has recently been suggested in the case of rubber that the molecules, because of their peculiar chemical structure, are helical in shape and elastic in themselves (Fikentscher and Mark, *Kautschuk*, **6**, 2 (1930)). In view, however, of the fact that elasticity is shown not only by polymerized isoprene but by polymers from such widely different molecules as methyl acrylate, styrene, vinyl acetate, sulfurized fatty oils, and by proteins, and that it can be caused to display itself in materials which are otherwise inelastic by the introduction of swelling agents or the application of heat, it is difficult to admit that the elasticity of rubber is referrable directly to the chemical structure of polymerized isoprene.

X-ray studies of stretched elastic colloids cannot yet be said to have solved the problem of the cause of elasticity in such materials. It is true that raw rubber gives an x-ray diffraction pattern at moderate elongations, indicating that certain parts of the material have assumed a definite configuration, but vulcanized rubber, which has better elastic properties, requires to be stretched much further before it gives such a pattern, while polyvinyl acetate showed no pattern at 1500 per cent elongation (Whitby, McNally, and Gallay, *Trans. Roy. Soc. Canada*, **1928**, Sect. III, 27) and polystyrene none at 1300 per cent elongation (Whitby and McNally).* It would seem that the regular orientation of parts which an x-ray diffraction pattern connotes is not essential to the possession of elastic properties. Indeed, the occurrence of such a pattern is rather to be regarded as indicating that the material is assuming the character of an inelastic fiber.

It has been suggested that an x-ray diffraction pattern can be obtained from stretched elastic colloids because there occurs on stretching a "de-swelling" of the higher by the lower of the two phases of which the material is assumed to consist. Such a "de-swelling" seems improbable. Even if the phases present are to be regarded as swelling each other, they are originally swollen to an extent far short of their maximum capacity for swelling, and it would seem unlikely that mere extension would produce a syneresis. Elastic colloids (*e. g.*, vulcanized rubber), after being caused to imbibe ten or more times their own weight of a liquid, can be stretched without any apparent occurrence of syneresis. And it does not seem likely that a syneresis on stretching could occur in raw rubber, where, on the view under consideration, the higher polymeric phase is swollen only slightly and where the "swelling agent" is itself a solid, *viz.*, the lower polymeric phase.

Vulcanization

It has already been stated that the elastic properties of the members of a series of polymeric products obtainable from a given monomer by a given means of polymerization depend on the degree of polymerization, and it has been suggested that in any such series there is an optimal degree of polymerization. This conception of the dependence of the elastic properties on the degree of polymerization is, the

* Hünemörder found a slight ellipticalness in the amorphous ring, indicating the incipience of a pattern, on stretching polystyrene to 4000 per cent.

author thinks, fundamental to an understanding of the phenomenon of vulcanization.

When a simple mixture of rubber and sulfur is heated, it goes through a number of stages. At first, as it comes from the mixing mill, it is soft and almost completely lacking in elasticity; after it has been heated for a certain length of time but before a "set-cure" has taken place, it will be found, if removed from the mould, to be still softer and completely inelastic; on continuing the heating, it undergoes a set-cure, but its elastic properties at this stage are relatively poor; as the heating is continued, it reaches the point of optimum cure, when the elastic properties are at their best; on heating still longer, it becomes overcured: the elastic properties become poorer, and finally the material becomes more or less brittle ("short") or, if the amount of sulfur is sufficient, leathery or hard. In the author's opinion, the gradual change from the soft mass onward essentially connotes increase in the degree of polymerization.

The writer encountered in the reaction-product of dianisidine (1 mol.) and crotonaldehyde (2 mols.) a case which illustrates rather strikingly the progression of the properties of a material through an elastic stage as the degree of polymerization increases. If the two materials mentioned are mixed, the reaction-product is at first a thin liquid; in allowing it to stand at room temperature, it passes, as polymerization progresses, through the stage of a viscous liquid, to (in the course of an hour or so) that of an elastic solid, then to that of a very tough but inelastic solid, and finally (after standing overnight) to that of a brittle solid.

The experimental study of the vulcanization of rubber presents many difficulties, owing to the insolubility of the material. In the face of these difficulties, the writer turned to a study of the vulcanization of fatty oils, with results which throw considerable light on the nature of the vulcanization process in rubber. The vulcanization of fatty oils under the influence of sulfur and heat is closely analogous to the vulcanization of rubber. In both cases the starting material, *viz.*, liquid fat on the one hand and broken-down rubber on the other, is lacking in elasticity; on heating for a sufficient length of time, the rubber undergoes a set-cure and similarly the oil-sulfur mixture undergoes gelation; on continued heating, the product goes through a series of changes in physical consistency: at first it is very weak; it then arrives at optimal elastic properties, and finally, if sufficient sulfur or accelerator is present, it becomes inelastic, being "short" or brittle in the case of rubber, "crumbly" in the case of oil.

An important respect in which the two processes are analogous is that the same organic compounds (dithiocarbamates, mercaptobenzothiazole, etc.) accelerate both. This is of particular significance, for, as Stevens has pointed out, "the profound effect of accelerators, particularly in the vulcanization of soft rubber, indicates that a solution of the vulcanization and accelerator problems may come simultaneously" (*J. Soc. Chem. Ind.*, **48**, 60T (1929)).

Following an earlier, general study of the action of sulfur on fatty oils (Whitby and Chataway, *J. Soc. Chem. Ind.*, **45**, 115T (1926)), the author has, in conjunction with Pasternack, investigated the action of organic accelerators on the vulcanization of oils, and has found that such accelerators appear to act as polymerization catalysts. On heating fatty oils, such as linseed, maize, perilla and Chinawood, with sulfur, a succession of changes is to be observed. Originally the oil is completely soluble in cold acetone; as heating proceeds, a portion becomes insoluble in that medium, owing to polymerization; as heating proceeds further, a portion becomes insoluble, not only in cold acetone but also in cold ether, and, shortly after the appearance of an ether-insoluble fraction, the oil sets to a solid. At first the solid

is extensible and elastic; on further heating, it loses its extensibility, but still appears as elastic when subjected to compression; finally, it becomes crumbly or hard and inelastic.

Now it was observed that if, after heating had been continued to a point at which a certain proportion of acetone-insoluble material had formed but at which no ether-insoluble was present, all free sulfur was removed by means of ether, the addition of organic compounds such as those used for the acceleration of rubber vulcanization reduced markedly the period of heating required to cause setting to an elastic solid.

There was a notable quantitative difference between linseed oil and Chinawood oil with regard to the effectiveness of organic accelerators in hastening the time of setting under the influence of sulfur and heat, the relative effect being greater in the latter than in the former case. In this connection it is worthy of note that Chinawood oil, which, as Boeseken has shown, contains a doubly conjugated system of linkages, was found to be converted into a solid by the addition of such typical polymerization catalysts as stannic chloride and antimony pentachloride, whereas linseed oil in its original condition was not so polymerizable. Linseed oil, however, became polymerizable by such catalysts, if it were heated for a certain length of time (short of the setting time) with sulfur. It would appear that on heating linseed oil with sulfur there takes place a change, probably in the arrangement of the double bonds, which renders it polymerizable by polymerization catalysts, among which it would seem vulcanization accelerators must be classed.

By analogy, then, with the vulcanization of oils, we arrive at the conclusion that the vulcanization of rubber involves polymerization as an essential feature and that vulcanization accelerators can act as catalysts in the polymerization. As in the case of linseed oil, it may be necessary, before such catalysts can function, for a preliminary change to be brought about in the material by means of sulfur and heat.

On the view that polymerization is the fundamental process involved in vulcanization, several further points may be noted as significant. (1) The formula for rubber put forward in Part I of this lecture shows the rubber molecule as possessing a terminal conjugated system. It is well known that the presence of such a system frequently confers on compounds the property of polymerizability. (2) The fact that benzoyl peroxide, well known as a polymerization catalyst (it was used, *e. g.*, for the preparation of polyvinyl acetate in the experiments on that material), as a vulcanizing agent for rubber is in accord with the view that vulcanization involves essentially polymerization. (3) The aging of vulcanized rubber may best be regarded as involving further polymerization of the rubber (with its concomitant effect on the physical properties) by means of atmospheric oxygen, also well known to be a polymerizing agent. The fact that hydroquinone retards the aging of rubber is in accord with this view, for hydroquinone is well known to be an anti-catalyst for polymerization. Hydroquinone will, *e. g.*, prevent the polymerization of acrolein (Moureu), of styrene (H. S. Taylor, private communication) and of certain other polymerizable compounds.

The author is indebted to J. G. McNally for making the measurements on the elastic properties of polystyrene and raw rubber given in Tables II–VII.

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The Appearance of Atmospheric Cracks in Stretched Rubber

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1. Introduction and Methods

It has been known for a long time that cracks often occur on the surface of rubber articles in use, especially if these articles are exposed to light. Thus air-brake hose, bicycle tires, and sealing rings occasionally show large cracks which may render the articles prematurely unusable. The appearance of these cracks is usually attributed to sunlight, as indicated by the expression, "sun-cracking," so frequently found in the literature.

The aim of the present investigation was to find the causes of the formation of cracks, to study systematically the influence of different factors on their formation and, if possible, to find means of preventing the appearance of cracks.

A complete survey of the literature is probably superfluous, since very recently an excellent summary by Evans[1] has appeared. However, a few articles should be mentioned briefly; above all that of Williams,[2] who has described the phenomena very clearly, and who distinguishes three types of oxidation of rubber:

1. Oxidation throughout the total mass of the rubber.
2. Formation of a film on the surface.
3. "Cracking" or "checking," *i. e.*, the formation of cracks.

1. Oxidation throughout the total mass of the rubber is characterized by a decline of the mechanical properties and an increase in weight, and is brought about most markedly by aging in the Geer oven or in the Bierer-Davis bomb. In spite of the considerable decline in the mechanical properties, nothing special is to be observed on the exterior, except incidental changes in blooming. The action of sunlight accelerates this oxidation also, but in our investigation this type of oxidation is not concerned.

2. With rubber strips, which have been stretched in sealed glass tubes containing air or oxygen under slight pressure (5%), Williams shows that under the action of sunlight a glassy, inelastic skin is formed on the surface. When the rubber is released, the presence of this film is evidenced by the wrinkling of the surface. Experiments with light of different wave lengths proved that ultra-violet light is not necessary for the formation of the film. This phenomenon is likewise of no particular concern in the present work.

3. The third type of oxidation, the appearance of cracks, is sharply distinguished from the other types by Williams. The great rapidity of the formation of cracks is characteristic, as is the much too often overlooked increase in weight. The presence of O is necessary but not that of direct light, for cracks are also formed on the shady side of the strips. Williams therefore attributes cracking to ozone, an idea which he supports by more detailed experiments. Furthermore, unstretched rubber is not attacked by ozone, even after a long time. The formation of cracks is greatest at low elongations, while at greater elongations the cracks become smaller.

Our investigation will deal principally with this third type of oxidation.

In the second place, the work of Shepard, Krahl, and Morris[3] should be mentioned. These investigators exposed to sunlight rubber samples stretched 12.5%. The largest cracks were formed at this degree of elongation, whereas with greater elongation the cracks were smaller, and in the unstretched condition the sample showed no cracking, even after one month. The influence of different factors on this phenomenon was studied further. The authors favor the idea that light is the cause of cracks.

Still other investigators like Krahl[4] and Evans[5] attribute the cracks to light, perhaps ultra-violet light. Recently Kearsley[6] has published a detailed study of the action of ozone on vulcanized rubber. We shall return to his results and observations later.

Method

As a start, vulcanized rubber strips 2 mm. thick and with 0, 2.5, 5, 10, 25, and 50% elongation were placed in a frame on the roof of the laboratory, at an angle of 45° to the horizontal and pointed toward the south. The strips were so placed that air had free access to both sides of the surface of the rubber. The great influence

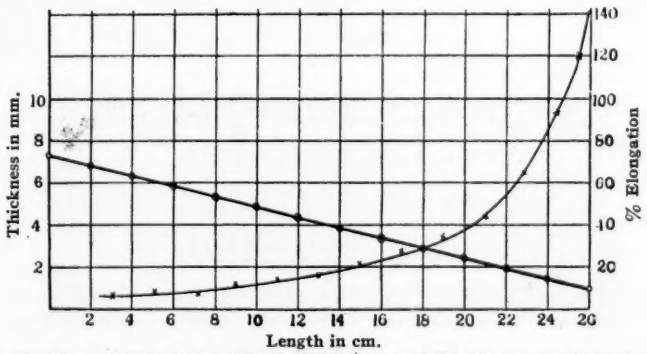


Diagram 1—Relation between Thickness and Elongation in % and Length of Wedge-Shaped Rubber Strips

of the degree of elongation showed immediately in the size and number of the cracks. It therefore appeared advantageous to use a new method of stretching.

Instead of strips of uniform thickness, wedge-shaped strips were now vulcanized, whose thickness varied from 8 to 1 mm., and with a length of 28 cm. With this method of stretching, the smaller the thickness the greater is the elongation, which in these experiments varied from about 8 to 100 per cent.

The elongation at every point of the wedge-shaped strips was determined by measuring the distance between two lines originally 2 cm. apart. Diagram 1 shows graphically the relation between thickness and elongation in per cent of the length. By the aid of this diagram the elongation at every point of the strips can be easily determined by interpolation. The great advantage of this method is clear; instead of stretching many strips, there is obtained in one strip a wide range of continuously varying elongation. Diagram 2 shows in more detail the apparatus for stretching these strips.

II. General Experiments on the Causes of the Formation of Cracks

1. Influence of Elongation.—In the first experiment a number of wedge-shaped strips of a simple high quality mixture were exposed to air in a stretched condition.

The mixture, designated hereafter as Mixture A, had the following composition:

First latex smoked sheet	100 parts by weight
Sulfur	5
Zinc oxide	3
Diphenylguanidine	1

and was vulcanized 10, 20, 30, and 40 min. at 147° C. (optimal tensile strength at 30 min.), so that the influence of the degree of vulcanization (see later) could be studied at the same time.

On the sample vulcanized 10 minutes a few isolated, relatively large cracks were formed when the elongation was low. With increasing elongation, the number of cracks increased, and in a definite range of elongation the surface of the rubber was entirely covered with large, deep cracks. This range is designated as "maximum," and lies from 10 to 20 per cent elongation. Above 20 per cent elongation, the size of the cracks became gradually smaller, while the number still increased. At about 90 to 100 per cent elongation the cracks were so small that they could hardly be seen with the naked eye.

Diagram 3 shows a wedge-shaped strip photographed under tension. The smallest tension at which cracks still appeared and the tension at the maximum are shown in Table I as they were determined with Mixture A after 5 days' exposure.

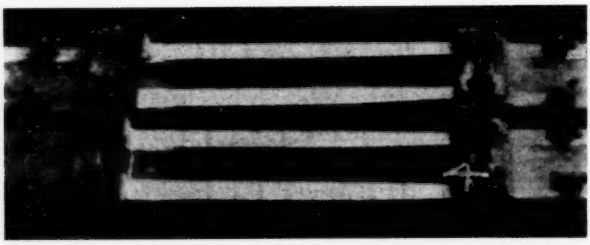


Diagram 2—Extension of Wedge-Shaped Strips

TABLE I

BEGINNING AND MAXIMUM OF CRACKING IN WEDGE-SHAPED STRIPS OF MIXTURE A AFTER 5 DAYS' EXPOSURE

	% Elongation			
	Sunny Side		Shady Side	
Vulcanizations	Beginning	Maximum	Beginning	Maximum
10 min.	8	11–13	6	9–14
20 min.	9	12–14	7	11
30 min.	Very small cracks	No clear maximum	No sharp maximum	No sharp maximum
40 min.	No cracks but film	....	Very small cracks	9–11

From Table I it follows that in a time of vulcanization of 10 and 20 min. the cracks on the shady side began to form at somewhat lower elongation while the maximum on the shady side was at somewhat lower elongation.

2. Influence of Sunlight.—The presence of cracks on the shady side leads one to conclude that direct sunlight is not essential to the formation of cracks, as has already been shown by Williams.[7] It may be possible that the cracks on the shady side are caused by reflected diffused light. That this is not the case was proved by an experiment in which a stretched wedge-shaped strip of Mixture A (vulcanization 10 min. at 147° C.) was exposed only at night. The experiment was made in De-

cember, 1929, when the strips were always completely in the dark from 5 P. M. until 7 A. M. on the roof, while by day they were kept in a dark cabinet. Nevertheless, within 9 nights completely normal cracks formed. The appearance of the cracks began at 9 per cent elongation, while the maximum lay at 10 to 14 per cent. As was to be expected, cracks formed on both sides of the strips in the same way, and, in fact, in the same manner that they are formed on the shady side. In Diagram 4 a part of the maximum of this strip at 13–14 per cent elongation is shown. This experiment has therefore proved conclusively that *sunlight either direct or indirect is not necessary for the formation of cracks.*

Certain components of the air therefore are the cause of the occurrence of cracks in stretched rubber, and later studies show that *ozone* is probably the cause. In this connection the term "sun-cracking" used until now is incorrect, and it is desirable to designate these as *"atmospheric cracks."*

Although sunlight is not the cause of the cracking, the action of light is nevertheless not wholly without influence on their formation. This influence is, however, more negative than positive; often smaller cracks occur on the sunny side than on the shady side. Obviously this difference is to be attributed to the formation of an oxidized skin on the sunny side, as has been described by Williams.

This oxidized skin is particularly striking in the case of high quality rubber mixtures, while with mixtures having a great deal of filler it is much less distinct (see later). It is best seen when the rubber is compressed somewhat. The presence of the skin is shown by a wrinkling of the surface. Upon closer observation one sees that very much smaller cracks have been formed, which, however, run in an arbitrary direction and are much less deep.

These phenomena were studied more closely on strips of a transparent rubber with the following composition:

First latex crepe	100
Tetramethylthiuramdisulfide	0.5
Stearic acid	1.5
Zinc oxide ("Kadox")	1
Sulfur	2

With strips of this mixture vulcanized at 147° C. for 25 and 40 min., cracks appeared only on the shady side after one week in the stretched condition in the open air, although on the sunny side an oxidized skin was formed.

Diagram 3—Wedge-Shaped Strips of Mixture A Vulcanized 10 Min. at 147° C. Shady Side after 8 Days in the Open. Natural Size

Because of its transparency, this mixture was very well suited to the making of microphotographs. Diagram 5A shows a photograph of the sunny side, magnified

24 times. The many small cracks can be seen running in an arbitrary direction. On the other hand, Diagram 5B shows the relatively large cracks on the shady side running perpendicular to the direction of elongation, magnified 24 times. Between the large cracks the surface of the rubber on the shady side is much less affected than the surface on the sunny side.

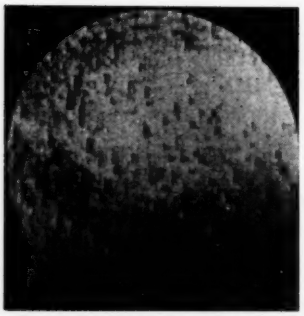


Diagram 4—Portion of a Strip of Mixture A after 9 Nights in the Dark in the Open. 13–14% Stretch. Magnified 3.1 Times

In Diagrams 5C and 5D the cross sections of the strips are shown perpendicular to the surface, magnified 32 times. Diagram 5C shows the cross section of the oxidized skin on the sunny side. The small cracks do not extend deeply into the rubber. Diagram 5D shows that the cracks on the shady side go much deeper.

The formation of the oxidized skin may be proved experimentally in another way. If a rubber strip which has been stretched and exposed to sunlight is released, it becomes very much bent, *viz.*, convex on the sunny side and concave on the shady side. This bending is a clear proof that on both sides of the strip unlike phenomena have taken place, and may be explained by the assumption that a layer has formed on the sunny side with more permanent deformation; therefore with less elasticity than in the rest of the strips. Diagram 6 shows the way in which strips of Mixture A, 2 mm. thick, which have been vulcanized for increasing times and exposed for

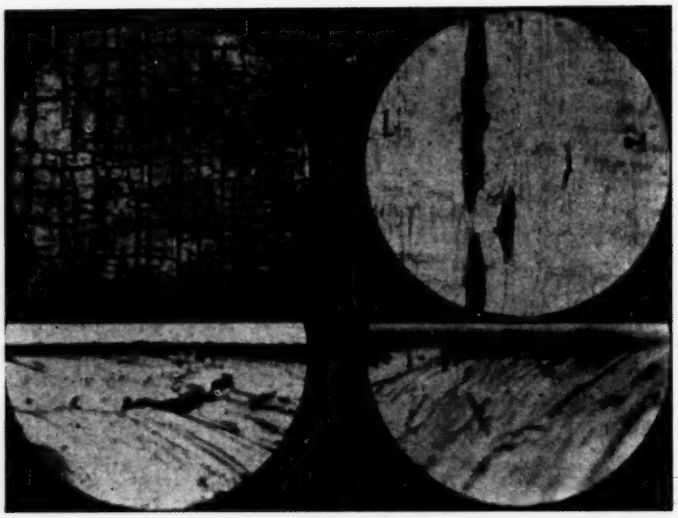


Diagram 5—Strips of the Transparent Mixture after a Week in the Open in the Stretched Condition. A. The Sunny Side Magnified 24 Times. B. The Shady Side Magnified 24 Times. C. Cross-Section of the Sunny Side Magnified 31 Times. D. Cross-Section of the Shady Side Magnified 31 Times

25 days with varying elongations, have become bent after being released. It follows from this that the degree of bending increases with: (1) Increasing degree of vulcanization; (2) increasing elongation.

That the atmospheric cracks do not result from cracking of the oxidized film is proved by the following experiment. An unstretched strip of rubber was exposed to the atmosphere. After two and one-half weeks no cracks had formed. Then the wedge-shaped strips were released in the usual way and kept in the dark. Even after three weeks no cracks had formed. One must conclude, therefore, that the air only forms cracks when the rubber is in a stretched condition.

3. Action of Ozone on Stretched Rubber.—As was shown in the preceding paragraphs, the formation of cracks is to be attributed to certain components of the air. Some experiments with a few gases will be reported, in the first place with ozone, which has already been designated by Williams as the cause of cracks. First of all, qualitative experiments were made in which the air was ozonized by means of a Heraeus mercury-quartz lamp. The lamp was enclosed in a wooden box and the ozonized air was admitted with a water jet vacuum into a desiccator covered with black paper in which the rubber samples in stretched condition were placed in darkness. With a wedge-shaped strip of Mixture A vulcanized 10 min. at 147° C., after $2^1/_2$ hours the formation of a few cracks could be detected. After

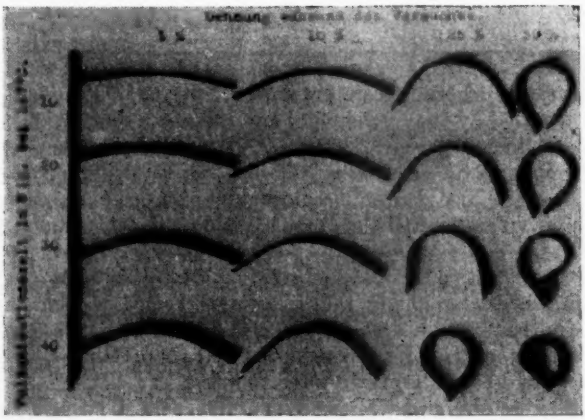


Diagram 6—Strips of Mixture A, with Varying Tension Exposed 25 Days in the Open, after release from Tension

10 hours the cracks corresponded very well with those formed during a week in the open. The cracks first appeared at 9 per cent elongation. The size of the cracks and their distribution over the surface corresponded very well with the phenomena observed on the shady side of the strips made in the open.

As a control, the ordinary air of the room was drawn through the desiccator. However, after a month no cracks were observed in a stretched strip of Mixture A. The formation of cracks by the air ozonized by the quartz lamp shows therefore that the idea of Krahl that ultra-violet light is necessary for the formation of cracks is erroneous.

In the organic chemical laboratory of the Technische Hochschule at Delft, further quantitative experiments were carried out. At first experiments were made with a large ozone apparatus of six ozonizers in parallel through which a current of dried oxygen was passed. A transformer carried a secondary current of 8000 volts. The oxygen, with an ozone concentration of about 8 per cent, was introduced through a wide glass tube containing the stretched rubber. When the current was turned on, the rubber showed very large cracks almost immediately. These

cracks were greatest at low elongations, and gradually became smaller with increasing elongation. The rubber was, however, much more strongly attacked than in the experiments in the open. Mixtures of very different composition were all attacked very greatly, and almost immediately.

In greatest contrast to these stretched strips was a strip of Mixture A in the unstretched condition. This still showed absolutely no cracks after 3 min., except on the edge of the strip, where a certain amount of deformation took place on account of cutting. It is therefore very evident that, even at this great concentration of ozone, *the deformation of rubber is a necessary factor in the formation of cracks.* This same fact was found by Haushalter,[8] and was also recently confirmed by Kearsley.

In this connection still another experiment was carried out. The wedge-shaped strips of rubber which had been exposed to the action of ozone in the unstretched condition were afterward stretched for 2 hours. Small cracks then appeared. As a result of this, it is evident that the ozone does not form an oxidized skin which tears as a result of the stretching. On the contrary, the action of ozone is to be explained only by the fact that the stretched rubber is in such a state that the ozone is able to attack it and form cracks.

Because of its very powerful action, the experiments at higher concentrations of ozone could not be compared to earlier experiments in the open air. Very much smaller concentrations of ozone were obtained by means of a simple ozonizer, in which air was ozonized by the discharge of an ordinary Rauhmkorff induction apparatus, through which a primary current of 2.5 volts and 0.4 ampere were led. With this apparatus it was possible to obtain a fairly constant concentration of 0.003 per cent ozone. The determination of the ozone content was done before the rubber strip was placed in the glass tube by leading the air through a potassium iodide solution.

At this low concentration, a stretched strip of Mixture A showed a few cracks after only 5 min. while after 30 min. the cracks were formed in about the same way as after a week in the open air. The determination of the ozone content of the air conducted over into the strips of rubber showed that about 90 per cent of the ozone originally present had been absorbed by the rubber.

Similar results were obtained with other mixtures. An unstretched sample also showed no cracks, with the exception of a few on the sides deformed by cutting.

Kearsley's explanation of the formation of cracks by the action of ozone is that a surface film is formed with very little strength. He also explains the formation of cracks in stretched rubber in air in the same way.

The experiments described above on stretched strips of rubber, after they had been exposed for a short time to ozone, prove without question that this explanation is untenable.

The correct explanation must, however, be left unsettled provisionally. It may be possible that the formation of cracks is related to the "crystallization" of rubber when stretched, but it is difficult to make it agree with the further facts indicated by x-ray investigations that crystallization only begins to appear at 80 per cent elongation.[9]

In any case, the rubber is converted into a particularly highly reactive state by as little as 10 per cent elongation, in which condition the ozone acts upon it.

The formation of cracks by ozone in stretched rubber shows similarities with like phenomena in metals. It is known that certain metals which are under tension are attacked in special ways by chemical agents, and even cracked. Thus, for example, brass under tension undergoes cracking[10] when it is immersed in mercury or a mercuric salt solution.

Although on the basis of experiments with ozone it is highly probable that ozone is the cause of cracking in the air, there is still the possibility that other gases in the atmosphere play a part in the formation of cracking. Small quantities of nitrogen oxides and sulfur dioxide have been proved to be usually present in the atmosphere. Therefore experiments were made with these gases and also with chlorine, which as a very reactive gas might act upon rubber in a manner similar to ozone.

The results of these experiments proved clearly that no cracks were formed in stretched rubber by the action of these gases. It is probably safe to conclude, therefore, that ozone in the atmosphere is the cause of the formation of cracking in stretched rubber.

In this connection it should be mentioned that until the present time the question has been disputed whether ozone is present on the earth's surface. Doubtless it is certain that ozone is present at great heights in the atmosphere. The ozone content of the upper atmosphere has been determined in a systematic way by Dobson[11] and his collaborators in recent years. From these investigations it follows that at a height of 40 to 50 kilometers above the surface of the earth a layer of ozone is found which, calculated at 0° C. and 760 mm. pressure, has a thickness of 3 millimeters. The quantity of ozone at our level is rather variable and decreases greatly with rise in atmospheric pressure.

It does not seem at all unlikely that very small quantities of ozone reach the earth's surface from this layer of ozone. In this connection it should be noted that in the experiments with stretched rubber the rapidity with which the cracks occurred was somewhat variable, and was especially great on windy days.

Probably the formation of cracks in stretched rubber under the influence of ozone represents a very sensitive and specific reaction of ozone, as Reynolds[12] recently observed. This investigator claims to have measured the amount of ozone present in the London air by chemical means.

III. Some of the Factors Which Influence the Formation of Cracks

The chief causes of the formation of cracks have been discussed in the preceding paragraphs; therefore the experiments will now be described in which the influence of various factors in the preparation and composition of rubber mixtures was studied.

The various factors may be classified as follows:

1. *Vulcanization:* (*a*) Degree of vulcanization; (*b*) other factors.
2. *Composition of the mixture:* (*a*) Raw rubber; (*b*) fillers; (*c*) softeners; (*d*) other ingredients.
3. *Chemical influences on the surface.*

1. Effect of the Degree of Vulcanization.—(*a*) The experiments already described also give an idea of the influence of the degree of vulcanization on the formation of cracks. In the experiments with Mixture A it was found that the largest cracks appeared on the undercured strips (time of vulcanization, 10 min. with 1.1 per cent combined sulfur), whereas the normally vulcanized strips (time of vulcanization, 20 min. with 1.8 per cent combined sulfur and time of vulcanization 30 min. with 2.3 per cent combined sulfur) smaller cracks were formed. In overcured strips (time of vulcanization, 40 min., and 2.9 per cent combined sulfur) the cracks on the shady side were still smaller, while the oxidized skin which has already been fully described had formed on the sunny side. These results do not agree with those of Kearsley, but they do agree, however, with those of Shepard, Krahl, and Morris.

In the face of these facts, the question may be asked, whether the relations between the degree of vulcanization and the extent of the cracking are a function of

the combination of sulfur or of changes in the mechanical properties of the vulcanizates. It was possible to answer this question by experiments with a few mixtures in which with increasing times of vulcanization the content of combined sulfur increased, but where the stress-strain curves showed nearly the same course.

Two mixtures—B and C—of the following compositions were prepared.

	B	C
First latex crepe	100	100
Sulfur	5	5
Titanium oxide	95	95
Zinc oxide	...	3
Diphenylguanidine	1	1

Both mixtures were vulcanized for increasing lengths of time—10, 25, and 40 min.—at 147° C. In Diagram 7 the stress-strain curves obtained with the Schop-

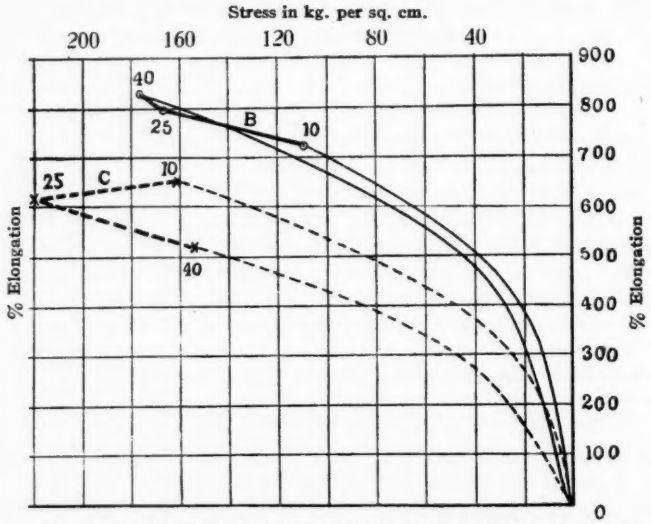


Diagram 7—End Point Curves of Mixtures B and C, Vulcanized for Increasing Times at 147° C. The Figures Give the Times of Vulcanization in Minutes

per dynamometer are reproduced graphically, while in Table II both the vulcanization coefficients and the moduli, *i. e.*, the stress at 600 per cent elongation are summarized. As is seen from Table II and Diagram 7, the course of the stress-strain curves of Mixture C is entirely different from Mixture B, obviously because of the "activating" influence of the small quantity of zinc oxide. In Mixture B the modulus is almost independent of the degree of vulcanization. In the case of Mixture C the modulus after a vulcanization of 10 min. is already greater than with Mixture B, whereas with longer time of vulcanization the modulus of Mixture C is still increasing considerably.

Table II shows that the time for the combination of sulfur in Mixture C was somewhat longer than for Mixture B.

Wedge-shaped strips of Mixtures B and C were then vulcanized for 10, 25, and 40 min. at 147° C., stretched and exposed to air. After a week it was found that in all strips of Mixture B relatively large cracks had been formed in practically the same way, without there being any effect due to differences in vulcanization coef-

ficients. With strips from Mixture C, the effect of the time of vulcanization was plainly evident. In strips vulcanized 10 min., somewhat smaller cracks formed than in Mixture B, corresponding to the somewhat greater modulus. The cracks in the strips vulcanized for 25 and 40 min. were still smaller. It was evident therefore that it was not the degree of vulcanization as such, but the character of the stress-strain curves which had a determinant influence on the size of the cracks.

A second confirmation of this view was found with the study of Mixture A, in which a Congo rubber was used instead of first latex sheet. The end-point curve of this mixture vulcanized for 10, 15, 30, 45, and 60 min. at 147° C. shows, as seen in Diagram 8, that here too the stress-strain curves for different times of vulcaniza-

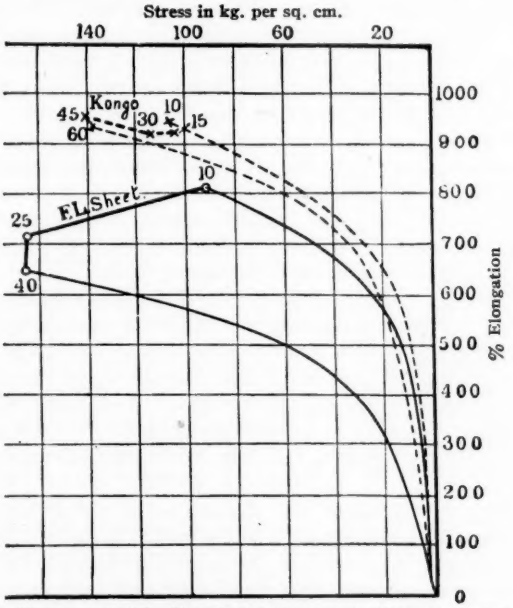


Diagram 8—The End-Point Curves of Mixture A with First Latex Smoked Sheet and Congo Rubber Vulcanized for Increasing Times at 147° C. The Figures Give the Times of Vulcanization in Minutes

tion are almost coincident, in contrast to Mixture A with first latex smoked sheet. The combination of sulfur proceeds, however, quite regularly, as Table III shows.

TABLE III

VULCANIZATION COEFFICIENTS AND MODULI OF MIXTURE A WITH FIRST LATEX SMOKED SHEET AND CONGO RUBBER

Vulcanization (Time in Min.)	Vulcanization Coefficients		Modulus in Kg. per Sq. Cm. (Stress of 600% Elongation)	
	First Latex Sheet	Congo Rubber	First Latex Sheet	Congo Rubber
10	0.8	...	25	16
15	...	1.7	...	17
25	2.1	...	77	..
30	...	2.6	...	19
40	2.8	...	118	..
45	...	3.6	...	21
60	...	4.4	...	22

With wedge-shaped strips of Mixture A containing Congo rubber vulcanized 10, 25, and 40 min. at 147° C., large cracks formed after a week's exposure under tension in the air. Also with the samples vulcanized 40 min. the cracks were as large as was observed only in the case of undercured strips, which again shows clearly the influence of the modulus on the formation of cracks.

The relation between the size and number of cracks and the modulus of the stretched rubber may be explained in the following way. If ozone acts upon stretched rubber, a crack results. The size of this crack depends upon the sensitivity of rubber to notching, and this in turn upon the modulus. With undercured rubber the resistance to notching is less, and consequently the cracks are larger, while with a higher degree of vulcanization the resistance to notching increases, and the cracks thus become smaller. When a crack forms, the tension is released within a certain distance of the crack, and therefore no new cracks form within this distance because there must be tension in order for the ozone to act. The smaller the cracks are, the smaller will be the distance in which the tension is released, and consequently the number of cracks will be greater.

From this it follows that with a low degree of vulcanization the number of cracks will be small on account of their size, while with increasing degree of vulcanization the number increases and the size becomes gradually smaller.

(*b*) *Other Factors.*—There remained the possibility that even during vulcanization certain stresses were formed in the rubber as a result of pressure and deformation, and that these gave rise to the formation of cracks after vulcanization. Accordingly a few slabs 2 mm. thick from Mixture A were vulcanized, in which indentations were made with nails during vulcanization. From these slabs strips were cut and were exposed in the open under no elongation and at 25 per cent elongation. After a week no cracks appeared in the unstretched pieces, showing that these indentations were without effect on the formation of cracks. In the indentations made by the nails on the strips at 25 per cent elongation very small cracks formed, smaller than in the normal parts of the strip. These phenomena can be explained in the following way.

If a rubber strip with progressively thinner parts is stretched 25 per cent, the thin places will be stretched more than 25 per cent. Measurements proved that in the case described here the stretch in the indentations made by the nails was 80 per cent when the whole strip was stretched 25 per cent. From previous knowledge of the relation between elongation and cracking it was concluded that in the thinner places with 80 per cent elongation smaller cracks would be formed than in the normal portions with 25 per cent elongation because this degree of elongation lies closer to the maximum (10 to 20 per cent).

Conversely, the strips can also be so stretched that the thinner places are stretched about 25 per cent. Under these conditions elongation of the whole strip was now 5 per cent, *i. e.*, such a small elongation that no cracks were to be expected. In the experiments large cracks formed in the thinner places, but there were no cracks in the normal strips, as is shown clearly in Diagram 9. This showed therefore that here no particular form of tension was involved, but rather that the degree of elongation of the rubber played the decisive part.

There still remained the possibility that the time of plasticization of the rubber might influence the appearance of cracking. Therefore two Mixtures A were prepared, in one of which the raw rubber was plasticized for 4 min., in the other for 60 min. With wedge-shaped strips vulcanized for 10 min. at 147° C., the cracks were quite similar after one week's exposure under tension, from which it follows that the plasticizing has no influence on the formation of cracks.

2. Composition of the Mixture.—(*a*) The kind of rubber used. First latex smoked sheet, first latex crepe, scrap crepe and earth crepe (two low-value qualities of *Hevea* rubber) and lastly a sample of Congo rubber and guayule were examined. These samples of raw rubber were tested in the form of wedge-shaped strips of the composition of Mixture A, vulcanized at 147° C. for 10, 15, and 45 min.

After a week in the open while stretched, cracks had formed in all the strips without exception, those in the undercured strips being the largest. The kind of raw rubber used does not therefore play the chief role in the formation of cracks.

(*b*) Fillers. In the course of the experiments, the influence of several fillers on the formation of cracks was studied. To Mixture A were added 20 per cent by volume of fillers: zinc oxide, zinc oxide (*Kadox* brand), lithopone, and gas black.

These mixtures were vulcanized as wedge-shaped strips for 10, 25, and 40 min. at 147° C. Cracks were formed in all the mixtures without exception, the largest cracks occurring in the undercured strips, while with increasing time of vulcanization the cracks gradually became smaller and more numerous. No specific influence of the filler was observed, not even in the mixture with gas black, although this mixture was black and the others were white. Very likely slight differences were due to a difference in the modulus. With all the mixtures the first cracks began at 8 per cent elongation, whereas the maximum lay between 10 per cent and 20 per cent. The formation of an oxidized skin on the sunny side was less pronounced with these mixtures containing fillers than with Mixture A. These results do not agree with those of Kearsley. It should be mentioned, however, that the technic of Kearsley's experiment was different.

Diagram 9—Strips of Mixture A; Normal Part 2 Mm. Thick, Stretched 5%, Thinner Part Stretched 25%. Cracks Only in the Thinner Part. Magnified 2.25 Times

(*c*) Softeners. As typical softeners, the following were studied: mineral rubber, tar, glue, stearic acid, vaseline, paraffin, ceresin, ozokerite (crude), and "Sunproof."[13]

Three parts by weight of these substances were added to Mixture A, and these mixtures were then vulcanized in wedge-shaped form at 147° C. for 10, 20, 30, and 40 min. After a week's exposure in the open the following observations were made.

Mineral rubber.—Very large cracks appeared on the shady side, greater than with the control Mixture A. A thick oxidized skin was formed on the sunny side. The addition of mineral rubber must therefore be regarded as a detriment, which agrees with the results of Shepard, Krahl, and Morris.

Tar, glue.—No effect by these substances on the formation of cracks was observed.

Stearic acid.—After a week the strips with stearic acid were slightly less attacked than the control strips. After 2 weeks no difference was observed. The stearic acid therefore offers only slight improvement.

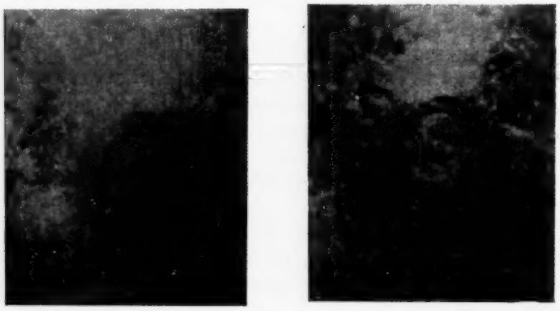
Vaseline.—The strips with vaseline after a week were also slightly less attacked than the control strips, but after two weeks were almost the same. Vaseline therefore does not improve the properties of rubber.

Paraffin, ceresin, ozokerite, and *"Sunproof."*—The strips with these substances were entirely without cracks after four weeks. It is surprising that these substances form an efflorescence or bloom on the surface of the rubber, and it is probably this bloom which protects the rubber against the action of the outer air.

Strips of the mixture containing paraffin, ceresin, ozokerite, and "Sunproof" were subjected to the action of ozonized air, as described above. It was found that the air containing 0.003 per cent ozone brought about a very distinct formation of cracks within 30 min. The limit of the ozone concentration must lie below 0.003 per cent, above which limit in this case the bloomed paraffin layer can no longer give protection.

It was also possible that the presence of swelling substances in the rubber might retard the formation of cracks. Therefore one per cent water, petroleum, and xylene were added to the mixture and the mixtures were vulcanized 10 min. at 147° C. However, stretching in the open showed no difference in the formation of cracks from the control strips.

Similar experiments were also made on the influence of accelerators (mercaptobenzothiazole, "Ureka," tetramethylthiuramdisulfide, diphenylguanidine), antioxidants ("Age-Rite Resin," "Stabilite"), and organic dyes (Vulkan Yellow G. N., Vulkan Green, Vulkafor Blue, and Vulkafor Red), but in all these cases cracks were soon observed in the wedge-shaped strips, which were exposed to the air under tension. Therefore no specific action of accelerators, antioxidants, or of coloring agents on the formation of atmospheric cracks could be found.



A B

Diagram 10—Cracks Formed around the Nail
A. Iron nail B. Aluminum nail

3. Chemical Influences on the Surface.—(*a*) Influence of iron compounds. In the course of the investigation it was observed several times that long cracks formed on the stretched strips along lines drawn in ink. This phenomenon may be due to two causes. (1) A chemical process, *e. g.*, a surface oxidation under the catalytic influence of iron compounds present in the ink, or (2), a physical process, that is, a difference in the degree of elongation caused by the scratching of the pen.

The experiment was therefore made with strips of rubber partially painted with ink, iron acetate, iron soap, and iron rust and stretched 25 per cent in the open air. Other strips were scratched with a dry pen and stretched 25 per cent. At the end of two days small cracks were observed in the strips, showing that on the strips painted with iron compounds cracks had formed in exactly the same way as on normal surfaces. No difference was observed in the size of the cracks, or in their distribution on the surface. With the strips scratched with the pen, however, longer cracks appeared along the scratches, as was also observed with the regular ink lines. These phenomena depends therefore upon the extent of the deformation.

The following phenomenon can be explained in the same way. It was observed that when a piece of rubber, nailed on wood, was exposed in the open air without

further elongation, a group of small cracks formed around the iron nail, as is shown in Diagram 10A. Here it was thought to be due to the action of the iron rust formed, but with an aluminum nail the same cracks were formed, as is seen in Diagram 10B. The origin of the cracks lies in the deformation of the rubber around the nail.

(*b*) Influence of Cu compounds. Williams gives a method of preventing cracks by immersing the rubber in a copper chloride solution. The oxidized skin formed by the action of the copper salt prevents the formation of acids.

William's experiment was repeated by immersing a wedge-shaped strip of rubber of Mixture A, which was vulcanized 10 min. at 147° C., in a one per cent alcoholic copper chloride solution. The strip was then stretched, together with a control strip, and exposed to the air. After one week the strip treated with copper was somewhat less attacked than the control strip, but after two and one-half weeks only a slight difference between the two strips was observed, as Table IV shows.

TABLE IV

CRACKS IN RUBBER TREATED WITH COPPER CHLORIDE

	Stretch in Elongation	
After 1 Week	Sunny Side	Shady Side
With copper	Cracks from 30% up Maximum about 40%	Cracks from 20% up No maximum
Control	Cracks from 14% up Maximum 16–26%	Cracks from 9% up Maximum 14–20%
After 2½ Weeks		
With copper	Cracks from 20% up Maximum 32–55%	Cracks from 16% up Maximum 20–32%
Control	Cracks from 10% up Maximum 16–25%	Cracks from 9% up Maximum 12–20%

It is evident from Table IV that treatment with copper does indeed displace the formation of cracks to higher elongations, but in no way prevents them.

IV. Summary

It was established that two factors are necessary for the formation of cracks: (1) stretching of rubber; (2) the action of ozone.

Experiments at night proved without doubt that light is not necessary for the formation of cracks, in fact it often has a negative influence as a result of the formation of a surface skin. The formation of cracks begins at about 8 per cent elongation and reaches its maximum, *i. e.*, the formation of largest cracks, which thickly cover the whole surface, at about 10 to 20 per cent elongation, above which degree of elongation the cracks become gradually smaller.

Artificially ozonized air causes the same cracks as the open air, only much more rapidly. Nitrogen oxides, sulfur dioxide, and chlorine form no cracks. Moreover, no cracks were formed in unstretched rubber subjected to the highest concentrations of ozone. The influence of sunlight or the light from a mercury quartz lamp is not necessary to the formation of cracks; in fact, an oxidized skin may be formed by the light, and this skin may even prevent the formation of cracks. Chemical factors, too, which promote the oxidation of rubber (iron and copper compounds) have no influence on the formation of cracks.

The influence of the degree of vulcanization on the formation of cracks is to be attributed solely to the mechanical properties, and indeed to the modulus of vulcanized rubber. The smaller the modulus the larger are the cracks.

The type of raw rubber or filler has no important influence on the formation of cracks, and accelerators, antioxidants, or organic dyes have just as little influence on

the kind and manner of formation of cracks. It should therefore be especially emphasized that the formation of cracks by the action of ozone is to be regarded as a typical property of stretched rubber.

Only the presence in the mixture of softeners which have the capacity for "blooming" can prevent the formation of cracks at very low concentrations of ozone.

The cases of cracking which take place in rubber articles which are exposed to atmospheric action can always be attributed to stretching of the rubber wherever cracks occur.

The foregoing investigation was carried out as part of the general rubber research of the combined rubber manufacturers of Holland. The investigation was begun during 1929, and the experiments were concluded at the beginning of 1930. Acknowledgment is here made to the directorates of the companies concerned for their ready agreement to the publication of this work. Our appreciation is also due Professor J. Boëseken and W. D. Cohen of the Organic Chemical Laboratory of the Technische Hochschule at Delft for their aid in the experiments with ozone and to T. W. Kingma Boltjes of the Microbiological Laboratory of the Technische Hochschule at Delft for his preparation of the microphotographs.

References

[1] *Trans. Inst. Rubber Industry*, **5**, 442 (1930).

[2] *Ind. Eng. Chem.*, **18**, 367 (1926).

[3] *Ind. Eng. Chem.*, **18**, 615 (1926).

[4] *Kautschuk*, **3**, 159 (1927).

[5] *Loc. cit.*

[6] *Rubber Age* (N. Y.), **27**, 649 (1930); *Kautschuk*, **6**, 244 (1930).

[7] *Loc. cit.*

[8] *India Rubber J.*, **70**, 897 (1925); Haushalter, Jones, and Schade, *Ind. Eng. Chem.*, **20**, 300 (1928).

[9] Katz, *Naturwissenschaften*, **13**, 410 (1925).

[10] Sacks, *Z. Ver Deut. Ingenieure*, **71**, 1511 (1927); *Mitt. Deut. Materialprüfungsamstalten, Sonderheft*, **5**, 144 (1929).

[11] *Proc. Roy. Soc. London*, **110**, 660 (1926); **114**, 521 (1927); **122**, 456 (1929); Harrison, *Nature*, **124**, 58 (1929); Ladenburg, *Naturwissenschaften*, **17**, 533 (1929).

[12] *J. Soc. Chem. Ind.*, **49**, 168T (1930).

[13] Offered to the trade by the Naugatuck Chemical Co. as a protective agent against cracking.

[Translated from Comptes Rendus des Séances de l'Académie des Sciences, Vol. 192, No. 16, pages 946–948, April 20, 1931.]

The Law of Degradation of Rubber Solutions as a Function of the Time at Different Temperatures

P. Bary and E. Fleurent

In *Comptes Rendus* (Vol. 184, p. 947, 1927) we showed that the molecular transformation of rubber due to heating at slightly elevated temperatures does not change the chemical composition of the rubber, and that the changes which were found are reversible.

When one works with rubber solutions at constant temperature, it is found that the viscosity of the solutions measured by the time of flow of a given volume through a capillary tube diminishes, more or less rapidly according to the temperature, as a function of the time, and may even reach very low values which approach those of the pure solvents. In this case the change which the rubber undergoes is often no longer reversible.

Although the viscosity measured in such solution does not have an exact physical meaning and depends upon the rigidity of the liquid, it nevertheless furnishes values directly related to the state of dispersion of the rubber in the solvent. Whatever may be the hypothesis for the structure of the disperse phase (polymerization, micelles of aggregated molecules, etc.), the reduction of the apparent viscosity corresponds to a degradation D of this structure which we shall represent by the expression $\frac{1}{\eta - 1}$, in which η is the viscosity of the solution in relation to that of the solvent taken as unity.

Some preliminary experiments at temperatures of about 20°, 40°, and 55° C. carried out for 5000 to 6000 hours have shown that the degradation of rubber in solution increases very rapidly with the temperature, and that in order to study the law followed as a function of the time it is necessary to maintain this temperature as constant as possible throughout the entire course of the experiment.

We therefore undertook a series of experiments on solutions of pale crepe (after extraction with acetone) in benzene, toluene, and xylene at the boiling temperatures of benzene and xylene and at 93.5° C. with the toluene, this latter temperature being maintained on a boiling water bath.

In expressing the values found for the viscosity during the entire course of the experiment as a function of the time in hours, we found that the curve obtained was correctly represented by the equation of a hyperbola:

$$(\eta - 1)(t + \theta) = A$$

The constant θ, which may be either positive or negative, depends upon the point selected for the beginning of the experiments. Unless the solution is homogeneous it is impossible to obtain measurements. Constant A is characteristic of the nature of the solvent and of the temperature of the experiment. In replacing $(t + \theta)$ by T and by substituting for the viscosity the degradation such as that defined above, one obtains:

$$T = AD$$

The values found in the experiments are given in the following table, where the last column indicates the length of time necessary for the solution to reach a viscosity at 15° 10 per cent greater than that of the solvent.

DEGRADATION OF RUBBER IN SOLUTION (2 G. PER 100 CC.)

Solvent	Temperature of Heating	A	T Calculated for $\eta = 1.1$
Benzene	80°	3540	35,400 hours
Toluene	93.5°	58.78	587.8 hours
Xylene	138–140°	18.15	181.5 hours

It should be mentioned that in the case of xylene the temperature appeared sufficiently high so that with the degradation there began a chemical change in the solution which acquired a dark red color and an odor which was distinctly different from the original odor.

We are carrying out the study of the phenomena thus described in a general way.

[Translated by K. Kitsuta from the Journal of the Rubber Society of Japan, Vol. 2, pages 389–397, 1931.]

Studies on the Thermochemistry of Rubber

I. Heat of Vulcanization of Rubber

Kyoichi Hada, Koichi Fukaya, and Takeji Nakajima

Recent studies on the thermochemistry of vulcanization of rubber by Blake (cf. *Ind. Eng. Chem.*, **22**, 737) are the most outstanding contribution in this field. Though there have been a few publications containing thermochemical data on the reaction between rubber and sulfur, such as those of Weber (*Chemistry of India Rubber*, pp. 106, 114), Seidle (*Gummi-Ztg.*, **25**, 710, 748), Williams and Beaver (*Ind. Eng. Chem.*, **15**, 255), Perks (*J. Soc. Chem. Ind.*, **45**, 142) and Kirchhoff and Wagner (*Gummi-Ztg.*, **39**, 357, 372), the vulcanization reaction is treated only in a qualitative way except by Weber, who worked quantitatively in the case of one sample. It should be said that it is of great value to have Blake's quantitative data of vulcanization for a whole system. Our work on the same subject gave widely different results from his, in spite of dealing with the same subject; the difference may be attributed to our different view in regard to the term *vulcanization*.

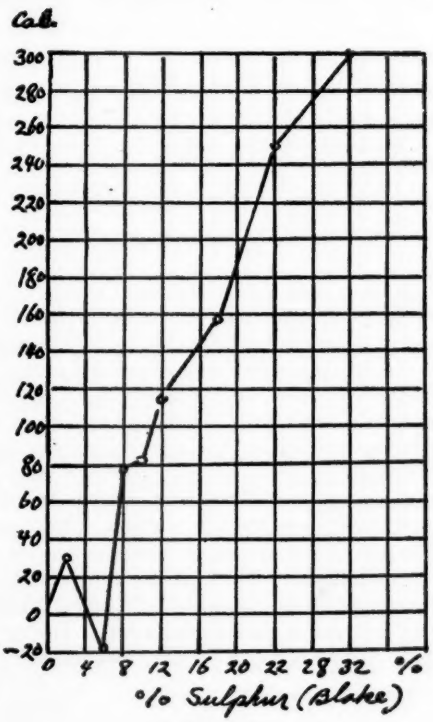


Figure 1

Blake obtained the heat of vulcanization of 10 samples containing sulfur from 0 to 32%, as shown in Fig. 1, which is based on the difference between the heats of combustion before and after vulcanization. The increase or decrease in the heat of vulcanization was irregular with respect to the amount of combined sulfur (compounded S) up to 6%, but above this porportion there was a steady increase in the heat of vulcanization as the proportion of combined sulfur increased. The heat of vulcanization obtained by Blake is then a resultant value of the following thermal effects:

(*a*) Heat of reaction between pure rubber and sulfur.
(*b*) Heat of reaction between resin and sulfur.
(*c*) Heat of reaction between protein and sulfur.
(*d*) Heat of combustion of free sulfur.

The vulcanization reaction described by Blake is interesting and valuable from the technical standpoint, but to ignore the heat effect of free sulfur is an omission from the scientific point of view. Though it is mentioned that the presence of free sulfur in rubber is negligible in effect (Scott and McPherson, Bureau of Standards Scientific Paper No. 22, p. 389), it is nevertheless right to consider that the sample containing 32% sulfur contains at least 1.5% free sulfur. The heat of combustion of sulfur is, according to Thomsen's Thermochemistry:

$$S_{amorphous}, O_2, O = 105{,}250 \text{ cal.}$$

Sulfur is considered to be amorphous when it is dissolved in rubber. The correction of the heat of vulcanization of Blake's sample containing 32% sulfur would be 45 calories, which would result in at least 10% error.

Experimental Procedure

Object and method: The object of this experiment was to find the heat of vulcanization between pure rubber and sulfur; accordingly, the method is different from that of Blake. Thus:

$[(C_5H_8)_x, S_y] = Q$
$(C_5H_8)_xS_y + (14_x + 3_y)0 = 5_xCO_2 + 4_xH_2O + ySO_3 + Q_1$
$(C_5H_8)_x + 14_x0 = 5_xCO_2 + 4yH_2O + Q_2$
$(S_{amorphous}, O_2, O, H_2O, Aq) = Q_3$
Heat of combustion of protein $= Q_4$
$(\text{Protein, S}) = Q_5$
$\therefore Q = Q_1 + aQ_2 + bQ_3 + c(Q_4 + Q_5),$

where a, b, and c is the weight in grams of pure rubber, sulfur, and protein, respectively, in a 1 gram sample. Q_4 is corrected from the heat effect of HNO_3 given off from the combustion of protein. No attempt was made to correct the thermal effect of the resinous substances contained in the sample, since the sample had been extracted with acetone. Though the complete extraction of resinous substances by acetone is difficult, it is believed that the variations due to the remaining resinous substance are within the experimental errors. Preparation of sample: The sample was prepared by vulcanizing at 40 to 50 pounds pressure for 2–15 hours. Simple mixtures of pure rubber and sulfur were used and the vulcanized samples were extracted with and kept in acetone. The acetone was removed by vacuum distillation before use, and, therefore, the sample should have contained no free sulfur.

Manipulation: The heat of combustion was determined as usual in a bomb calorimeter, with the necessary correction. The pure rubber was prepared by dissolution and fractional precipitation. The protein was removed by trichloroacetic acid. The results are tabulated as follows:

TABLE I
SAMPLES

No.	Proportion of S per 100 Pts. Rubber	Pressure of Vulcanization, Lbs.	Time of Vulcanization, Hrs.	Combined Sulfur, %	Rubber, %	Protein, %	Ash, %
1	3	40	2	0.750	95.350	3.136	0.173
2	3	40	4	1.703	95.014	3.106	0.171
3	7	40	4	2.935	93.823	3.067	0.169
4	10	40	6	5.924	90.934	2.973	0.164
5	20	50	4	13.350	83.756	2.738	0.151
6	30	50	4	17.510	79.735	2.607	0.144
7	30	50	15	23.611	73.834	2.414	0.133
8	40	50	15	27.707	69.878	2.284	0.126

TABLE II

HEAT OF COMBUSTION (FOR 1 GRAM)

Sample	Heat of Combustion						Average
1	10,587	10,587	10,459*				10,587
2	10,520	10,263*	10,470				10,495
3	10,211*	10,302	10,316				10,309
4	9,844	9,797	9,722				9,787
5	8,781*	8,788*	8,891	8,928		8,935	8,917
6	8,979	8,904	8,940				8,941
7	8,930	8,954					8,942
8	8,673	8,690	8,711				8,691
Protein	4,706	4,692					4,699
Protein-sulfur compound			5,207				5,207
Pure-Rubber	10,398*	10,540	10,432*	10,480	10,483	10,475	10,495

Average heat of combustion was taken from these data without * mark. Heat of combustion of protein is 5012 on ash-free basis.

TABLE III

SULFUR IN BURNED GASES

Sample	Wt. S Oxidized to SO_3 from a 1 Gram Sample	Wt. S Oxidized to SO_2 from a 1 Gram Sample
1	....	...
2	1.239; 1.510	0.271
3	2.545; 2.750	0.205
4	4.260	....
5	1.1425; 1.178	0.035
6	15.82; 16.54	0.72
7	21.09; 21.36	0.27
8	24.90; 25.46	0.56

TABLE IV

HEAT OF SOLUTION OF SULFURIC ACID

Sample	Empirical Formula	Molecular Ratio of Water per 1 Molecule of SO_2 Formed by Combustion	Heat of Solution of Sulfuric Acid Formed from 1 Gram-Molecule of Sulfur
1	$(C_5H_8)\ S_{0.143}$	224 H_2O	17,710
2	$(C_5H_8)\ S_{0.303}$	160 H_2O	17,520
3	$(C_5H_8)\ S_{0.526}$	61 H_2O	16,980
4	$(C_5H_8)\ S_{0.91}$	29 H_2O	16,600
5	$(C_5H_8)\ S_{2.6}$	12 H_2O	15,350
6	$(C_5H_8)\ S_{3.6}$	9 H_2O	14,660
7	$(C_5H_8)\ S_{5.2}$	6 H_2O	13,100
8	$(C_5H_8)\ S_{6.5}$	5 H_2O	12,180

TABLE V

CORRECTED HEAT VALUE OF SULFUR (CAL.)

Sample	For 1 Gram Sulfur					Corrected Heat Value of Sample
	(SO_2)	(SO_2, O)	(SO_3, H_2O)	(H_2SO_4, Aq.)	Total	
1	2279	1003	665	552	4499	33.7
2	2279	1003	665	538	4485	76.4
3	2279	1003	665	529	4476	131.4
4	2279	1003	665	518	4465	264.5
5	2279	1003	665	479	4426	590.9
6	2279	1003	665	457	4404	771.1
7	2279	1003	665	408	4355	1028.3
8	2279	1003	665	408	4327	1198.9

These results indicate that when the samples are burned in oxygen, all the sulfur changes to sulfuric acid. All calculations are, therefore, based on the assumption that all the sulfur changes to sulfuric acid. Thus:

$(S_{amorphous}, O_2)$ = 73,090 cal/1 gram-molecule sulfur
(SO_2, O) = 32,160 cal/1 gram-molecule sulfur
(SO_3, H_2O) = 21,320 cal/1 gram-molecule sulfur

Therefore (S, O_3, H_2O) = 12,750 cal/1 gram-molecule sulfur

TABLE VI

HEAT OF COMBUSTION OF PROTEIN (CAL.)

Sample	Contents in 1 Gram Sample Nitrogen, G.	Protein, G.	Amts. HNO_3 Formed (G.)	Heat of Formation of HNO_3	Heat of Solution of HNO_3	Heat of Combustion of Protein	Corrected Heat Value
1	0.0050	0.0314	0.0225	5.6	2.0	157.2	164.8
2	0.0050	0.0310	0.0225	5.6	1.8	155.7	163.1
3	0.0049	0.0307	0.0211	5.4	1.8	153.7	160.9
4	0.0048	0.0297	0.0216	5.3	1.8	149.0	156.1
5	0.0044	0.0274	0.0198	4.9	1.6	137.2	143.2
6	0.0042	0.0241	0.0189	4.7	1.5	130.7	136.9
7	0.0039	0.0241	0.0176	4.3	1.5	121.0	126.8
8	0.0036	0.0223	0.0162	4.0	1.5	114.5	120.0

TABLE VII

HEAT OF REACTION BETWEEN PROTEIN AND SULFUR (CAL.)

Sample	Contents in 1 Gram Sample Protein, G.	Sulfur G.	Heat of Combustion of Protein	Heat of Combustion of Sulfur	Heat of Combustion between Protein and Sulfur	Heat of Reaction
1	0.0314	0.0031	157.2	10.2	179.6	−12.2
2	0.0310	0.0031	155.4	10.2	177.6	−12.0
3	0.0307	0.0031	153.7	10.2	176.0	−12.1
4	0.0297	0.0030	149.0	9.9	190.3	−11.4
5	0.0274	0.0026	137.2	8.9	156.7	−10.6
6	0.0261	0.0026	130.7	8.6	149.4	−10.1
7	0.0241	0.0024	121.0	7.9	138.0	− 9.1
8	0.0228	0.0023	114.5	7.6	130.7	− 8.6

The calculation of the heat of vulcanization of the rubber-protein system is made from the following equations mentioned already:

$$Q = Q_1 + aQ_2 + bQ_3 + c(Q_4 + Q_5)$$

Where Q is the heat of vulcanization:

Q_1 is the heat of combustion of samples (Table II)
aQ_2 is the heat of combustion of compounded rubber (Calcd. from Table I and II)
bQ_3 is the heat of combustion of compounded sulfur (all corrections of heat of formation and solution of sulfuric acid are made from Table III and IV)
cQ_4 is the heat of combustion of protein in compounded rubber (all corrections of heat of formation and solution of nitric acid are made from Table VI)
cQ_5 is the heat of reaction between protein and sulfur (Table VII)
The signs of the heat effects are then as follows:

Q_1	Q_2	Q_3	Q_4	Q_5
−	+	+	+	−

Calculation of the heat of vulcanization was as follows:

TABLE VIII

CALCULATION OF THE HEAT OF VULCANIZATION

Sample	Q_1	Q_2	Q_3	Q_4	Q_5	Q
1	10,587	9,992	34	165	−12	−393
2	10,495	9,957	76	163	−12	−287
3	10,309	9,832	131	161	−12	−173
4	9,787	9,529	265	156	−11	174
5	8,918	8,777	591	143	−11	604
6	9,941	8,355	771	137	−10	332
7	8,942	7,737	1,028	127	− 9	−41
8	8,691	7,323	1,199	120	− 9	−40

This result is shown in Fig. 2.

Discussion

The results indicate that the vulcanization of soft rubber is an endothermic reaction, the value of which decreases with increase in the vulcanization coefficient.

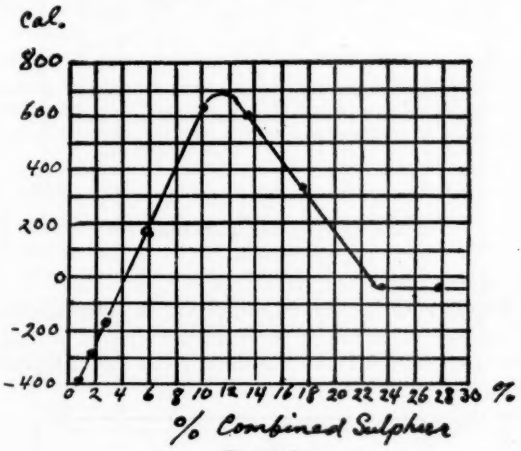


Figure 2

This reaction changes to exothermic and reaches its maximum value at about 12% combined sulfur, whereupon it decreases gradually with increase in the vulcanization coefficient and becomes an endothermic reaction with the formation of ebonite, a great difference from that of Blake. Our result may not, however, be absolutely correct in some of the following points: (1) The heat of combustion of pure rubber was 10,495 calories, which is close to that of Blake's value (10,547), but there is still some doubt of there being some impurities when it is compared with that of Messenger (*Trans. Inst. Rubber Industry*, **5**, 71), who gave 10,970 calories on extremely highly purified rubber. (2) There is a possibility of an error in that the value of the heat of combustion of sulfur is not our own determination, but is taken from the data of others.

Nevertheless the fact cannot be denied that there is a general tendency for a change from a minimum heat of reaction to a maximum, and then a gradual decrease to a constant value.

Two explanations can be given to explain the difference from the result of Blake: (1) The vulcanization of soft rubber is slower in the interior, since the cross-section

of vulcanized rubber showed more separation of sulfur inside. (2) Although there are some differences in reaching the maximum internal temperature by the different

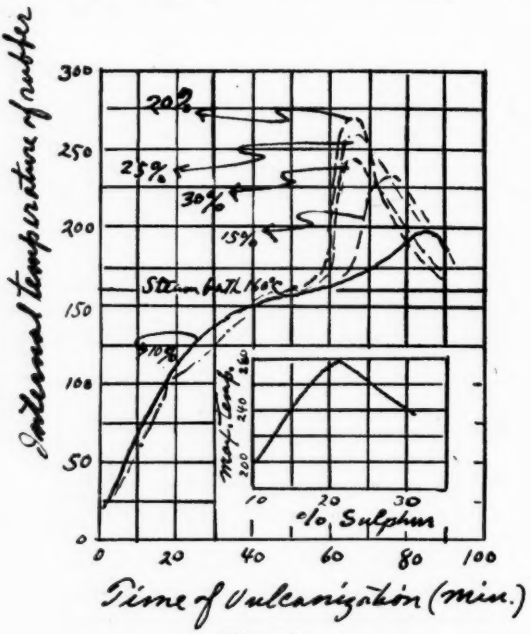


Figure 3

sulfur contents of rubber during the vulcanization as determined by different investigators, the internal elevation of temperature showed a maximum (Fig. 3) with increased sulfur content. There was, however, a fall in temperature with the

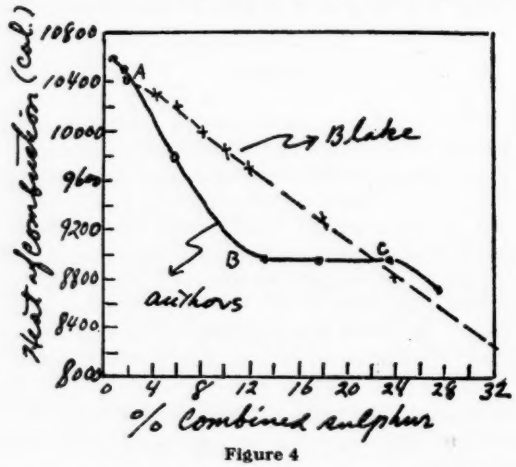


Figure 4

formation of ebonite. This fact cannot be attributed to the change in heat ductivity due to the change of composition, because the heat conductivity of rub

is 0.00032 and that of sulfur 0.00012, but to the lowering of the heat of vulcanization itself.

The main difference from the result of Blake is then dependent upon the content of resinous substance (although Blake made no explanation of the above fact).

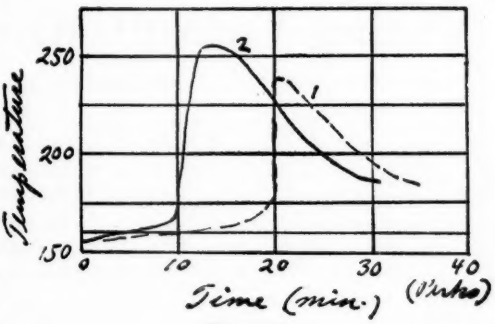


Figure 5

A comparison of the heat of combustion of samples with that of Blake, as shown in Fig. 4, shows a greater value in Blake's samples which contain 2–22% sulfur; A, B, and C (Fig. 4) must be attributed to the difference in the content of resinous substance. That such an idea is correct is also shown by the following facts: (1) The acetone extract was around 5% for samples of lower combined sulfur contents, and about 3% in ebonite, but the samples containing about 16% combined sulfur showed around 10% extract, with some variations. (2) The results of Perks and Williams, as shown in Figs. 5 and 6, respectively, show clearly that the presence of resinous substances has

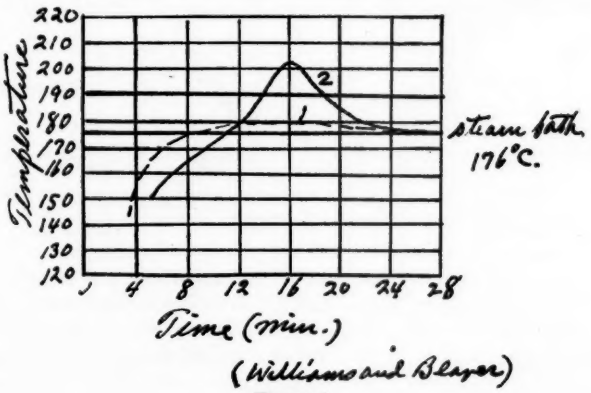


Figure 6

a great influence on the change in the internal heat during vulcanization. Curve 1 represents the result of experiments after the extraction of the resinous substance with acetone, in curve 2 there was no such treatment. Both were vulcanized under the same conditions. The result of Williams stands out strikingly in this respect.

Summary

1. The heat of vulcanization of the system: pure rubber-sulfur is determinated.
2. The absolute value of the experimental data is in doubt, however, since the results were widely different from those of Blake.
3. The experimental results are discussed.
4. The results of Blake are discussed.
5. The difference from the results of Blake is attributed to the difference in the content of resinous substances in the sample.

[Translated by K. Kitsuta from the Journal of the Rubber Society of Japan, Vol. 2, pages 251–254, 1930.]

Studies of the Heat of Reaction during Vulcanization of Rubber

Yasushi Toyabe

It has been known that there is an evolution of heat during vulcanization, by some unknown mechanism, but so far no quantitative data are available on this subject, owing perhaps to the technical difficulties in studying the phenomena of heat evolution which may give a clue to the true process of vulcanization. The author started this experiment with the idea of obtaining results by the application of a combination of analytical chemistry and experimental thermal data, as it is difficult to attack the problem directly by the use of thermochemistry alone. Further work is in progress and will be reported elsewhere.

Method of experimentation and discussion: (1) The effect of the heating medium on the change of temperature of pure rubber.

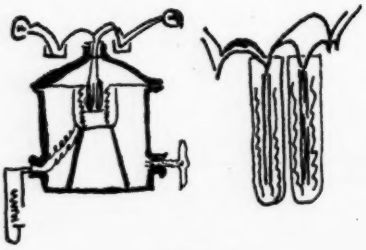


Figure 1

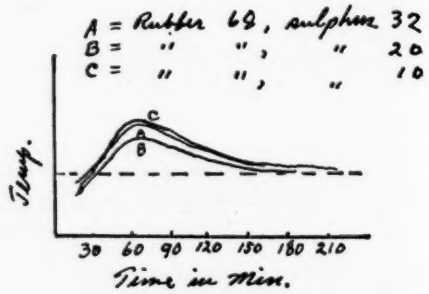


Figure 2

During the determination of the heat of vulcanization, the sample must be in contact with some kind of gas, as it is difficult to design an apparatus to avoid gaseous contact of the sample. Studies on the change of temperature of rubber and gases in contact with it was made by a thermo-couple during the heating of rubber, with the object of finding whether the gases in contact with the rubber are thermally active. It is thought that the gases with the lowest heat-inertia are the ideal ones for use. The results of studies showed that nitrogen had nothing to do with the thermochemical change, but air, carbon dioxide, and hydrogen caused the elevation of heat. Accordingly nitrogen was used for this purpose.

(2) Rubber-sulfur mixture. Since the heat of vulcanization is not great, it necessitates an accurate determination and special attention must be taken in keeping the volume of sample constant throughout; inserting the thermometer bulb in the center of the sample-mass, for instance, caused an uneven distribution of heat and led to experimental errors (cf. *J. Soc. Chem. Ind.*, **28**, 1441).

To bring about uniform heating of the sample and heating medium without any great difference in temperature from lack of uniformity of sample necessitates a special apparatus (cf. *J. Soc. Chem. Ind.*, **33**, 316). The apparatus was made of a glass desiccator with a capacity large enough to contain a small electric furnace, in which stood two test tubes—one containing the sample and the other asbestos

fiber—both connected by an electric thermo-couple, as shown in Fig. 1. Vulcanization was carried out in nitrogen gas. The changes of temperature determined during the vulcanization are shown in Fig. 2. The change of temperature at the center of sample showed a curve of rapid elevation when heating started, then a

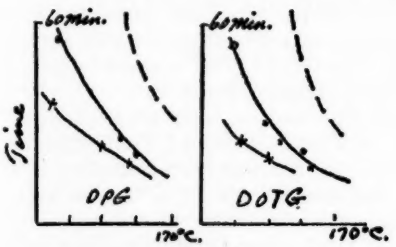


Figure 3

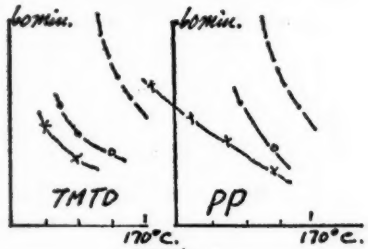


Figure 4

slow rate for a while, then a maximum temperature, and finally a gradual decrease in the logarithmic curve until it reached the temperature of the heating medium. One of the most interesting facts found in this experiment is that all three samples compounded with 68 parts rubber and 32, 20, and 10 parts sulfur, respectively, showed the maximum point at the same time when the temperature of the heating

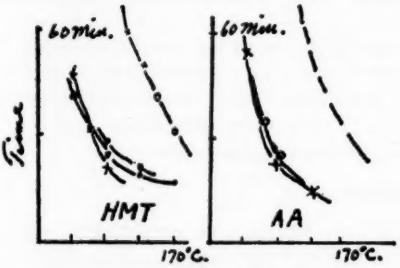


Figure 5

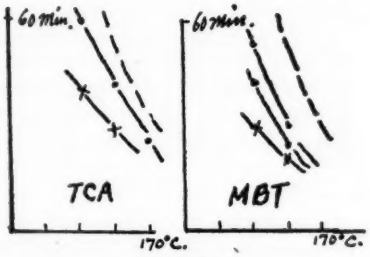


Figure 6

medium was the same. Another interesting fact is that approximately one-half of the total sulfur was found to be in a combined state when it approached the maximum point of the curve, and this relation was not changed by a change of compound nor by a change in the vulcanization temperature (Table I).

TABLE I

Compounding		Temperature of Vulcanization					
		155°		196°		170°	
Rubber	Sulfur	Time to Max. Point, Min.	F.S./T.S., %	Time to Max. Point, Min.	F.S./T.S., %	Time to Max. Point, Min.	F.S./T.S., %
68	32	60	56.0	35	49.7	20	47.8
68	20	60	61.5	..	..	20	46.6
68	10	60	59.8	..	..	20	39.1

F. S. = Free sulfur, T. S. = Total sulfur.

(3) The effect of organic accelerators. The effect of organic accelerators is shown in Fig. 3. The effects of accelerators are in general as follows:

(*a*) In the presence of accelerators, the maximum point of the curve is reached in a very short time, and the values are greater.

(*b*) When the result is expressed in a curve by plotting the time of reaching the maximum point as the ordinate and the temperature as abscissa, the curve approached the abscissa.

(*c*) When the mixture contained no accelerators, all curves were in one place, without any relation to the amounts of compounding ingredients added, but in the presence of accelerators the curves generally approached the abscissa when the sample contained less sulfur.

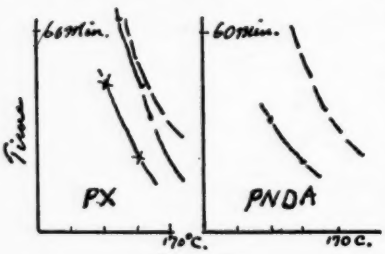


Figure 7

(*d*) This position is not always related to the ordinary activity of the accelerators-*e. g.*, with hexamethylenetetramine it was in the shortest and "PX" in the longest time.

(*e*) Accelerators are classified in 4 groups from the appearance of the curves.

I. "AA," hexamethylenetetramine. Same position of curves, regardless of variation in sulfur content.

II. Diphenylguanidine, di-*o*-tolylguanidine. Directions of the change of curves are greater as the sulfur varies.

III. "TCA," "PP," "PX." Same as above except the rate of curve was small.

IV. "MBT," tetramethylthiuramdisulfide. The change of rate curve and direction was generally small.

Vulcanized samples with accelerators were taken when the maximum points of the curve were reached, and analyses were made. The results were nearly the same as those of Table I, showing that the combined sulphur remained approximately 50% of the total sulfur, though there were some differences in the vulcanization coefficients, because of the rapid increase in temperature.

Conclusion

The results of experiments indicate that an addition of accelerators caused the change of molecular arrangement of the rubber hydrocarbon. This discovery is of a great value in explaining the mechanism of acceleration, which is different from physical, chemical, and physico-chemical theories proposed heretofore.

[Translated by K. Kitsuta from the Journal of the Rubber Society of Japan, Vol. 2, pages 236–238 1930.]

The Determination of the Chloroform-Soluble Substance of Vulcanized Rubber

Iwasaburo Minatani and Ichiro Aoe

The determination of the chloroform-soluble substances in vulcanized rubber is a valuable clue to the content of certain ingredients, such as asphalt, mineral rubber, pitch, etc., for vulcanized rubber containing these ingredients shows a greater proportion of chloroform-soluble substance. Vulcanized rubber containing none of these materials generally has a chloroform extract of 0.3–3.0 per cent. It is generally high in uncured rubber, but even optimum and highly vulcanized rubber contains some chloroform-soluble substance. This fact was pointed out by Tuttle and Weber, in the Official method edited by the German Industrial Material Committee, and in a report of the Joint Rubber Insulation Committee (*Ind. Eng. Chem.*, **9**, 310; **6**, 80). The object of the experiments was to determine the chemical nature of the chloroform-soluble substances in vulcanized rubber, as it is not known whether they are hydrocarbons or their derivatives, and whether they have the same composition at the different stages of vulcanization. As the chloroform-soluble substance in vulcanized rubber containing none of the softeners mentioned above is obtainable only in small quantities, special attention was given in compounding of the rubber, and the following formula was used:

Raw rubber	100
Barytes	100
Sulfur	5
Light calcined magnesia	10

The raw material used was white Ceylon crepe and the barytes was added to avoid tackiness of the product, as was found in the undercured rubber. The mixture was pressed in thin sheets and vulcanized for 20 to 300 minutes at 147° C. and 50 lb. pressure. Nine sheets (0.3 × 22 × 22) of samples thus prepared indicated that a vulcanization of 40–50 minutes showed the best mechanical test. Determinations of acetone- and chloroform-soluble substances, free sulfur, and sulfur, fur, carbon, and hydrogen in the chloroform-soluble substance, were made within a week after the preparation of the sample. The material for extraction was cut into small pieces and passed through a 25-mesh sieve. Acetone extraction was carried out for 10 hours, using 2-gram samples in a Neffler apparatus, then 4 hours of chloroform extraction was made after the acetone extraction. The sulfur in the chloroform- and acetone-soluble substances was determined by oxidizing with fuming nitric acid and bromine water and weighing as barium sulfate. The carbon and hydrogen of the chloroform-soluble substances were determined by Pragle's micro-analysis method. The results are tabulated as follows:

Time of Vulcanization, Min.	Acetone Extract, %	Free-Sulfur, %	$CHCl_3$ Extract, %	Sulfur in $CHCl_3$ Extract, %	Carbon in $CHCl_3$ Extract, %	Hydrogen in $CHCl_3$ Extract, %
20	3.03	1.61	3.90	1.41	87.37	11.45
30	2.07	1.11	0.88	..	83.33	11.09
40	1.96	0.92	0.90	..	82.75	11.39
50	2.52	0.97	0.63	3.92	78.99	10.53

Time of Vulcanization, Min.	Acetone Extract, %	Free-Sulfur, %	$CHCl_3$ Extract, %	Sulfur in $CHCl_3$ Extract, %	Carbon in $CHCl_3$ Extract, %	Hydrogen in $CHCl_3$ Extract, %
60	1.38	0.07	0.52	4.23	82.36	11.16
80	1.47	0.14	0.60	3.89	...	...
100	1.27	0.06	0.43	6.10	80.57	11.10
200	0.98	0.04	0.71	3.39	...	...
300	0.95	0.04	0.91	4.23	82.89	11.54

Theoretical content of pure rubber: C = 88.24%, H = 11.76%. Content of acetone- and chloroform-soluble substance and free sulfur are given in percentages of original sample, but the carbon, hydrogen, and sulfur contents of the chloroform-soluble substance are given in percentages of chloroform extract.

The results indicate that the acetone-soluble substance and free sulfur gradually decreased as the time of vulcanization increased; the chloroform-soluble substance, on the other hand, showed the same tendency to decrease as the time of vulcanization increased up to 60 minutes, but increased again beyond 60 minutes. The color of the chloroform extract showed a gradual increase from yellow to reddish-brown as the time of vulcanization passed beyond the optimum point, beside, it lost its characteristic smell of rubber and became strongly pungent; this is attributed to the formation of resinous substances. The sulfur content in the chloroform-soluble substance depends on the amounts of chloroform-extract; it ranged from 0.022 to 0.055% of the original substance. It is not clear whether it was derived from the residue of acetone extraction or was formed by oxidation or by decondensation of rubber. It is difficult to dry the chloroform extract for the determination of carbon and hydrogen. In this experiment, the chloroform was evaporated off on the water bath at 70°–80° C. for 5 hours in darkness. It was then kept in a desiccator for 20–25 hours.

The chloroform extract of the rubber vulcanized 20 minutes appeared to be pure hydrocarbon, and was very sensitive to oxidation—the sample gave 87% hydrocarbon at the beginning, and only 85% when it was kept in a weighing flask for 4 days. An increase in the time of vulcanization caused an increase in the resinous substances, and analysis showed a lower carbon content in such material. However, it did not oxidize further, indicating that the substance is oxidizable immediately to some extent, but not beyond a certain limit. There were some differences in composition between the chloroform extracts of the first 4 hours and the next 10 or more hours of extraction. The first extract consisted of pure hydrocarbon, but the second one gave a composition C = 81.34%, H = 10.94%, which became insoluble in chloroform after drying. This phenomenon was observed in material which had undergone excessive vulcanization beyond the optimum point, and the chloroform-insoluble complex compound was formed by the decondensation and oxidation of the chloroform extract.

To sum up the results above, the chloroform extract was in highest proportion in undercured samples, and it approached a minimum at the point of optimum vulcanization, beyond which it again showed an increase. The composition of the extract from the uncured rubber was pure hydrocarbon which corresponded to the formula C_5H_8, but as the increase in the time of vulcanization caused a formation of resinous substance which was also evident by the appearance of the extract, an increase of chloroform extract in such case was not as great as was expected, and the percentage of carbon and hydrogen did not show any great variation beyond a certain limit.

[Translated from Kautschuk, Vol. 7, No. 5, pages 94–97, May, 1931.]

The Problem of the Action of Selenium in Rubber Mixtures

H. Rimpel

HAMBURG

When in 1926 Boggs and Follansbee[1] published their interesting studies on selenium, the discovery that selenium has an extraordinarily favorable effect on the resistance to abrasion of vulcanizates was of the greatest interest to rubber technologists, for the resistance to abrasion of rubber vulcanizates such as rubber tires and other products is of vital importance. It is not to be wondered at, therefore, that the question was immediately raised whether the enormous quantities of selenium which the rubber industry would probably require would be obtainable for all. Several years have passed since that time without a shortage of selenium. As a matter of fact, up to now selenium has been used in the rubber industry only in relatively small quantities. In 1929 only 50,000 kilograms of selenium were used by the rubber industry, which represents only about one-fifth of the world production. The actual reason for this lack of consumption has not been generally understood until now.

The writer, too, has from the first attempted to make use of selenium in order to obtain a greater resistance to abrasion. It was soon evident that something was wrong, and that in all events the addition of selenium to correctly vulcanized mixtures did not produce a greater resistance to abrasion. In order to settle this problem conclusively, a series of systematic experiments was begun. In this connection the method of measuring the resistance to abrasion was of decisive importance. Boggs and Follansbee carried out their experiments on abrasion with all the apparatus known at that time, and they obtained values which agreed very well.[2]

However, all of these tests were based on the same principle, namely, merely a measurement of the volume worn away. Anyone who has made abrasion tests of rubber products probably knows that the volume lost depends to a great extent upon the hardness and the coefficient of friction of the particular type of rubber, and that one cannot obtain comparable results with rubber products of different types as long as only the volume losses are compared.

The writer himself has carried out numerous experiments according to this method, and at the same time checked them by practical road tests. In all cases he has been forced to the conclusion that the practical results do not agree with the results on the abrasion machine.

Williams[3] was the first to utilize the "work" factor in calculating the relative resistances to abrasion, and thus make possible a comparison of different types of rubber products with one another. The Williams method, as is known, consists in measuring not only the volume losses but also the work expended in this abrasion, and calculating the volume which is worn away with an expenditure of one horsepower-hour. Moreover experiments with the Williams abrasion machine have shown that not only do the results agree when repeated, but also the practical abrasion experiments of auto tires, rubber heels, and such products have always agreed with the results on this machine. The Grasseli abrasion machine constructed according to the principle of Williams therefore seemed to be particularly suitable for a conclusive test of the results of Boggs and Follansbee.

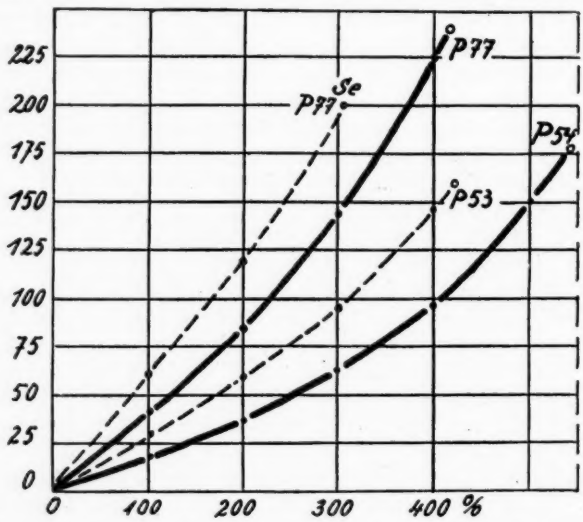
As a beginning, the following mixtures were used to test the action of selenium.

	I	II	III	IV
Smoked sheet	100	100	100	100
Sulfur	5	3	5	3
Selenium[4]	...	3	...	3
Zinc oxide	50	50	50	50
Magnesium oxide	1	1	...	...
Diphenylguanidine	...	...	0.5	0.5

By obtaining different cures, the optimum time of vulcanization was ascertained and the resistance to abrasion of these samples with the optimal quality was determined by the Williams method.

	Cure		Tensile Strength in Kg. per Sq. Cm.	Ultimate Elongation, %	Hardness (Shore)	Abrasion Loss in Cc. per Hp.-Hr.
	Minutes	Pressure (Atmosphere)				
I	40	$3^1/_2$	118.2	630	53	
	50	$3^1/_2$	160.5	670	53	420
	60	$3^1/_2$	164.5	650	52	
II	30	$3^1/_2$	138.8	620	51	
	40	$3^1/_2$	153.0	630	55	308
	50	$3^1/_2$	137.2	620	54	
III	20	3	183.0	640	55	
	30	3	228.4	630	56	304
	40	3	250.1	610	60	
IV	15	3	207.6	580	57	
	20	3	236.2	600	60	305
	30	3	204.2	540	59	

These abrasion tests led to the following conclusions. In mixtures without organic accelerators selenium does increase the resistance to abrasion, but only to the same extent as can be obtained by an organic accelerator. On the contrary, in mixtures with organic accelerators selenium has no effect upon the abrasion.



It might be objected that in the experiments above selenium did not exert its full effect because the selenium acted solely as an accelerator, since those accelerators which bring about a true combination of rubber and selenium (litharge, *p*-nitrosodimethylaniline, etc.) were lacking in these experimental mixtures.

In order to exclude any source of error, a few mixtures were tested which Boggs and Follansbee had themselves used, *viz.*, their P53, P54, and P77[5] mixtures.

	P54	P53	P77	P77 Se
Pale crepe	225	225	30	30
Smoked sheets	225	225	30	30
Zinc oxide	510	510	10	10
Gas black	....	....	24	24
Ozokerite	15	15	1.80	1.80
Diphenylguanidine	....	....	0.45	0.45
Tetramethylthiuramdisulphide	1.13	1.13	....	....
"808" accelerator	....	....	0.45	0.45
Sulfur	18	18	2.40	2.40
Selenium	....	6.75	....	1.50
Vulcanization min./atm.	40/3	10/3	60/3	40/4

After the mixtures were vulcanized according to the directions of Boggs and Follansbee, their stress-strain curves were determined:

	P54	P53	P77	P77 Se
Cure (min./atm.)	40/4	10/3	60/3	40/4
Stress at				
100% elongation	18.7	31.8	41.0	64.5
200% elongation	36.2	61.8	84.0	120
300% elongation	62.6	95.7	144.5	195.5
400% elongation	93.2	148.8	226.0	.....
500% elongation	150	.....	.....	.....
Tensile strength	177.4	158.1	237.5	199.0
Ultimate elongation in %	540	420	410	310
Hardness (Shore)	64	71	75	80
Specific gravity	1.672	1.686	1.172	1.188
Abrasion in cc./hp.-hr. at 22° C.	339	309	259.7	298.1

These tests show several important features. (*a*) The addition of selenium brings about a very decided stiffening of the stress-strain curve, which is also manifest by a 7 to 10 per cent greater hardness in the vulcanizate.

(*b*) There is no improvement in the resistance to abrasion by the addition of selenium.

(*c*) In most cases the addition of selenium diminishes the tensile strength (about twelve per cent).

(*d*) The addition of selenium brings about a distinct contraction of the mixture, which is manifest by a higher specific gravity, a phenomenon to which Kirchhof was the first to call attention, and which is also probably the cause of the greater hardening and the stiffening of the stress-strain curve by the selenium.

An attempt was then made to determine when the contraction of the mixture containing selenium occurs, whether it is only during the cure or previously. To this end, the specific gravities of the corresponding mixtures with and without selenium were determined before vulcanization as well. The mixture was sheeted out very smoothly on the rolls and the specific gravity was determined for a very thick sample from such a slab. As is evident from the following comparison of the specific gravities of this mixture in the vulcanized and unvulcanized states, this contraction takes place in the unvulcanized state.

	Without Selenium	With Selenium
Unvulcanized	1.232	1.255
Vulcanized	1.250	1.282

With the use of suitable inorganic accelerators, *i. e.*, with a shorter time of vulcanization, selenium also has no particular influence on the resistance to abrasion, as is shown by the following experiments with litharge-carbon black mixtures.

	I	II
Smoked sheet	100	100
Litharge	30	30
Sulfur	5	3
Selenium	...	3
Gas black (Cabot)	40	40

	Cure 15 Min. at 3 Atm.		Cure 20 Min. at 3 Atm.		Cure 30 Min. at 3 Atm.	
	Without Selenium	With Selenium	Without Selenium	With Selenium	Without Selenium	With Selenium
Stress at						
100% elongation	31.6	31.2	33.8	31.0	37.4	38
200% elongation	73.0	66.7	79.7	72.3	90.4	76.1
300% elongation	134.7	125.8	143.8	131.0	160.0	130.8
400% elongation	210.1	190.9	216.3	200.1	227.4	192.0
Tensile strength	281.0	260.3	249.0	234.5	258.0	218.5
Ultimate elongation in %	430	480	450	440	440	440
Hardness (Shore)	69	70	70	71	71	71
Abrasion in cc./hp.-hr.	312/25°	311/25°	328/23°	327/23°	309/23°	308/23°
Specific gravity	1.29	1.31	.....	.....	.....	.....

The tests with the litharge-carbon black mixtures agree with the preceding tests in that the addition of selenium causes no increase in resistance to abrasion, and the corresponding values agree approximately with those of the mixture without selenium. The addition of selenium on the contrary brings about no stiffening of the stress-strain curve of the litharge-gas black mixture, but rather the opposite effect. There is, however, a notable increase in the specific gravity. The rather large reduction in the tensile strength should be noticed.

For comparison this experiment was repeated with lamp black.[6]

Cure	15 Min. at 3 Atm. Without Selenium	15 Min. at 3 Atm. With Selenium	20 Min. at 3 Atm. Without Selenium	20 Min. at 3 Atm. With Selenium	30 Min. at 3 Atm. Without Selenium	30 Min. at 3 Atm. With Selenium
Stress at						
100% elongation	20.8	21.4	21.4	23.2	26.6	21.2
200% elongation	45.7	49.6	56.4	59.1	65.8	60.8
300% elongation	91.4	98.2	107.2	110	117.6	114.7
400% elongation	153.1	152.5	163.7	168.6	172.9	170
500% elongation	225.7	.....	...	...	...	...
Tensile strength	232.0	225.3	218.3	182.4	192.3	187.8
Per cent ultimate elongation	520	490	470	420	430	430
Hardness (Shore)	61	62	62	63	63	63
Specific gravity	1.250	1.282	...	...	...	...

This series of experiments shows that in mixtures containing lamp black accelerated with litharge, there is no stiffening of the stress-strain curve. Therefore, it is not the black, but the litharge which causes this behavior on the part of selenium, or, in other words, the stiffening effect of selenium is found particularly in mixtures cured with organic accelerators.

It might still be maintained that the stiffening of the stress-strain curve was a result of the accelerating action of selenium. A further test, however, proved the incorrectness of this idea, for the addition of a larger proportion of accelerator or of a more powerful accelerator did not bring about a corresponding stiffening.

Then again it appeared possible that if selenium had the effect on the resistance to abrasion believed by Boggs and Follansbee, such an effect would be manifest to a particularly high degree in mixtures which were vulcanized exclusively with selenium. In fact, it might also be thought that perhaps a combination of selenium and sulfur brought about this effect. It was of interest to put to a test the first possibility. To this end mixtures were chosen which were based on those used by Boggs and Follansbee.[7]

	B14		B14/1	
Pale crepe	24		24	
Whiting	30		30	
Zinc oxide	12		12	
Litharge	6		6	
Selenium	3.4		..	
p-Nitrosodimethylaniline	1		..	
Sulfur	..		1.2	
Cure (min./atm.)	40/3	60/3	15/3	20/3
Tensile strength (kg./sq. cm.)	76.7	73.3	95.1	86.8
Per cent ultimate elongation	360	360	420	400
Hardness (Shore)	64	64	69	69
Specific gravity	1.840	....	1.804	....
Abrasion (cc./hp.-hr. at 23° C.)	1400	1478	1199	1175

This experiment therefore agrees in its essentials with the results obtained with mixtures vulcanized with a combination of sulfur and selenium.

The experiments may be summarized in the following manner.

1. The extraordinarily great increase in the resistance to abrasion by the addition of selenium, which was found by Boggs and Follansbee, could not be verified.

2. In the presence of sulfur, selenium has a rather strong accelerating effect on vulcanization, and, therefore, it increases the resistance to abrasion of unaccelerated slowly cured mixtures, but to no greater degree than is brought about in the normal way by organic accelerators through shortening of the time of vulcanization.

3. Rubber-selenium vulcanizates without sulfur show no greater resistance to abrasion than rubber-sulfur vulcanizates.

4. In mixtures cured with sulfur and an organic accelerator, selenium brings about a distinct stiffening of the stress-strain curve and at the same time a contraction of the volume, which has already been observed by Kirchhof and which is evident in an increase in the specific gravity. In mixtures accelerated with litharge, this stiffening does not occur, but there is a contraction of the volume.

To what extent selenium has any influence on the resistance to flexing (the fatigue phenomenon) of vulcanized rubber, a property which has recently been attributed to it, is to be the object of a further investigation.

References

[1] *Trans. Inst. Rubber Industry*, **2**, 272 (1926).

[2] *Ibid.*, **2**, 290 (1926).

[3] First presented before the Rubber Division of the American Chemical Society at Richmond, Va., April 14, 1927.

[4] The selenium was from the firm of L. Marquandt A.G., Beuel a. Rhein, and before use it was finely pulverized in an agate mortar and then sifted.

[5] *Trans. Inst. Rubber Industry*, **2**, 291 (1926).

[6] The "Elastik" black of Gottfried Wegelin was used.

[7] *Trans. Inst. Rubber Industry*, **2**, 276 (1926), Compd. "B."

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Isoprene and Rubber[1]

Part 25. The Homologous Polymeric Hydrorubbers

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Harries states in his studies on natural and artificial kinds of rubber[2] "It would be of great importance to be able to carry out the reduction of rubber, because hydrorubber probably distills unchanged in a high vacuum, and therefore its constitution could be determined for certain."

This reduction was studied simultaneously by Pummerer and Burkard[3] and by Staudinger and Fritschi.[4] It is necessary to refer again to these works in order to correct earlier data on the basis of more recent experimental knowledge.[5]

1. Hydrogenation by Staudinger and Fritschi

In this investigation rubber was reduced at 270°, *i. e.*, in the fused state, in the presence of platinum by means of hydrogen under pressure. The hydrorubber obtained yielded, contrary to the opinion of Harries, a high molecular colloidally soluble hydrocarbon which showed the characteristics of a paraffin. From this it was concluded that rubber must be of high molecular weight and be composed of macromolecules. In the first communication on this subject,[6] it was stated that the particles of hydrorubber are visible in the ultra-microscope. This is not correct; long colloid molecules cannot be detected by the ultra microscope,[7] since they reach the wave length of visible light in one dimension only and in the two other dimensions they possess only molecular dimensions, unlike the colloid particles of suspensoids. The visible particles originate in the above case from the catalyst, which is very difficult to remove in colloid dispersion. On the basis of studies with the ultra-microscope, we assumed at first that a colloid was present, and that the molecular weight determinations which indicated a molecular weight of from 3000 to 5000 were incorrect.[8] We believed that the depressions observed in the freezing point depended upon impurities of adsorbed low molecular substances. The fact is just the opposite, however; the visible particles are due to impurities and the molecular weight determinations are correct, because the hydrorubber obtained by heating is a hemicolloid, of which the relatively low average molecular weight can be determined by cryoscopic measurements.[9]

2. Hydrogenation by Pummerer and His Collaborators

Pummerer and Burkard carried out the reduction in a very dilute hexahydrotoluene solution with platinum as catalyst. They described their hydrorubber as a substance which is converted into isorubber II and which contains hydrogen combined in a very unstable way.

These results could not be confirmed by Peter,[10] who proved that the hydrorubber obtained had the same chemical properties[11] as the product obtained by Fritschi at 270°.

Pummerer and Koch[12] reduced rubber with a large excess of platinum and obtained a hydrorubber of a paraffin character. Pummerer, Nielsen, and Gündel then confirmed the fact that this hydrocarbon is stable, and that no dehydrogenation

to an isorubber takes place.[13] However, this product also varies from that produced by Staudinger, Fritschi, and Peter in one essential property. According to the authors, it can be distilled unchanged in part, and indeed the distillate should have the composition $(C_5H_{10})_{10}$. This discovery forms an important confirmation of the theory of Pummerer that rubber has a low molecular weight. These results, however, could not be confirmed[14] in repeated experiments by Huber[15] and Schaal.[16]

The Crystallized Hydrorubber of Pummerer and Koch[17]

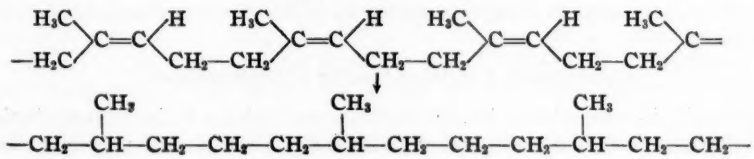
Pummerer and Koch prepared thoroughly purified rubber in crystalline form, and the hydrorubber prepared from such well purified products also crystallized. According to the knowledge of the crystallization of organic compounds of that time, this appeared to indicate a low molecular structure for both rubber and hydrorubber, since it was often believed earlier that high molecular organic compounds could not be crystallized. The crystallization of rubber upon stretching, which Katz[18] proved by studies with x-rays, indicated likewise.[19] These concepts are, however, incorrect, as was proved for example in the case of polyoxymethylene,[20] gutta-percha,[21] and other compounds. The atoms can orient themselves into a lattice structure of macromolecules[22] of unequal lengths but symmetrically constructed and these molecules are arranged in the crystallite as a bundle of parallel rods of differing lengths. The observations of Pummerer and Koch show only that the authors had a pure, therefore homogeneous, polymeric rubber and hydrorubber, respectively.

Pure rubber, unlike balata and gutta-percha,[23] is prepared only with difficulty,[24] which depends upon the fact that the rubber hydrocarbon has a much higher molecular weight than balata and gutta-percha.[25] Balata and gutta-percha have an average molecular weight of 50,000; unchanged rubber an average molecular weight of about 200,000.[26] Solutions of 0.1 *N* (0.68%) of the former are still sol solutions, whereas rubber solutions of the same concentration are on the contrary already gel solutions. The pure hydrocarbon can be obtained from dilute balata solutions by precipitation with alcohol, since normally dissolved molecules are present in this case. Protein is co-precipitated with rubber solutions, for in gel solutions the molecules do not move freely, and therefore it is hardly possible to remove the protein.[27]

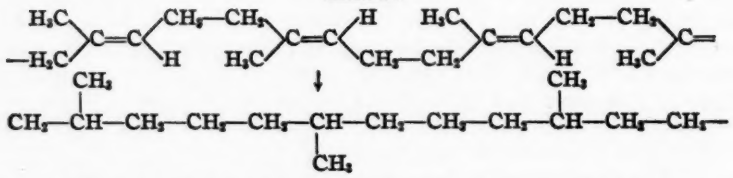
The difficulty in obtaining crystallized rubber cannot be due therefore to the structure of the molecules alone but also to the fact that it is difficult to produce pure, *i. e.*, homogeneous polymeric, rubber. A more or less strong cyclization[28] of rubber results easily upon hydrogenation, therefore, irregularities are present in the chains and hinder crystallization.

Moreover diastereoisomeric modifications of hydrorubber are possible. Rubber on the one hand and gutta-percha on the other hand are *cis-trans*-isomers,[29] whereas rubber has the *trans*, and balata and gutta-percha the *cis*-form. In the reduction they should therefore form *d*-astereoisomers.

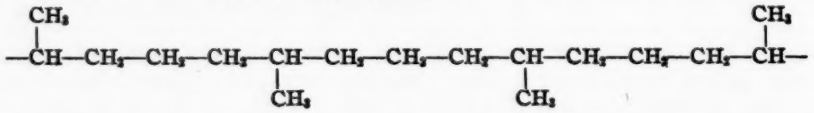
Gutta-percha and Balata:



Rubber:



It is possible that only a hydrorubber which is made up uniformly of the *trans*-form can be crystallized. It is further probable that in the reduction rearrangements in the chain occur, especially at higher temperature and unsymmetrically constructed molecules are formed, for example:



With unsymmetrically formed molecules of this type the atoms can no longer arrange themselves in a lattice-like manner and so the crystallization fails to take place.

From the ability of a high molecular substance to crystallize conclusions can be made only with regard to the similarity of structure of the molecule and not with respect to its length.

Hydrogenation of Harries

Finally the hydrogenation of rubber was also described by Harries,[30] who reduced solutions of masticated rubber, and found that rubber can be very easily reduced in this form, so that one does not need to work only in very dilute solution such as with the methods of Pummerer and Burkard. Harries based this process on the following considerations: "Later the idea came to me that the absorption of hydrogen by rubber is only a function of its dispersion or aggregation. Therefore, I plasticized the raw rubber to a high degree directly on the rolls. From such plasticized rubber it can be assumed, according to viscosity measurements,[31] that it no longer shows the original dispersed phase or the aggregate, but that it is disaggregated. Probably the mechanical plasticization disturbs or prevents the mutual absorption of two or more disperse phases which, according to Wo. Ostwald, are present in the usual natural rubber. Mechanical plastication therefore in this case leads to a similar end effect, like the peptizing action of an organic acid.[32] This consideration may be theoretically correct or not; in any case it has proved successful in practice."

The observation of Harries may be explained today in an entirely different way. In mastication the macromolecules of rubber are split up, the molecular weight diminishes greatly, in fact from about 200,000, the molecular weight of unchanged rubber, to 10,000 to 30,000, that of masticated rubber.[33] One per cent solutions of unchanged rubber are highly viscous gel solutions, one per cent solutions of masticated rubber are on the contrary sol solutions with low viscosity. Since in these latter the molecules move freely in contrast to gel solutions, the reduction proceeds much more easily.

Homologous Polymeric Series of Hydrorubbers

The earlier investigations[34] have already shown that the hydrorubbers obtained by the different methods are not wholly identical. The chemical properties of the

various products are, to be sure, exactly alike;[35] thus they are all stable to bromine, they are not attacked by oxidizing agents like concentrated nitric acid and potassium permanganate, and give no coloration with tetranitromethane.[36] Accordingly, they act like saturated paraffin hydrocarbons.

In appearance and in physical behavior, however, the products obtained by the different methods show great differences. The hydrorubbers obtained at 270° by the method of Fritschi are sirupy substances, of honey-like consistency. They dissolve rapidly in organic solvents and give solutions of low viscosity. The products obtained in solution at low temperature by the method of Pummerer have the appearance of purified rubber; they are therefore solid and yet somewhat elastic. They dissolve slowly in organic solvents, swell somewhat before dissolving, and the solutions are highly viscous.

Since similar changes in the physical properties of homologous polymeric series[37] of polyprenes[38] and polysterenes[39] with increasing length of the chains are found, it is possible to explain the differences in the various hydrorubbers in a simple way. The hydrorubbers obtained at high temperature without solvent have a relatively low molecular weight. They possess an average molecular weight of 2000 to 10,000, and are hemi-colloidal in character. They give, therefore, solutions of low viscosity, which obey the Hagen-Poiseuille law. The sphere of action of their molecules is relatively small, so that 3–5 per cent solutions are still normal solutions, *i. e.*, sol solutions.[40] The products obtained in solution at lower temperature have a very high molecular weight, *i. e.*, an average molecular weight of 20,000 to 30,000. These higher molecular hydrorubbers give solutions of high viscosity; 3–5 per cent solutions are already gel solutions which show slight deviations from the Hagen-Poiseuille law, which depends upon the length of the molecules in the case of molecular colloids,[41] as has been proved before.

With other high polymeric compounds, the physical properties of the series of hydrorubbers are governed by the length of the chains. They depend upon the magnitude of the intermolecular forces.[42] In order to explain the characteristic properties of high polymers, no special hypotheses are therefore necessary as, for example, those of special forces of association and of the micellar structure of the colloid particles, as has been the case up to now.

Just as gutta-percha and its decomposition products may be considered representative of the homologous polymeric series of polyprenes, so hydrorubbers may also be assumed to be a homologous polymeric series of polypranes, though they are not true products of polymerization. The various members of the polyprene and polyprane series can be characterized as entirely similar in the average degree of polymerization, calculated on the C_5 group. The following table shows that in the series of polypranes, just as with the series of polyprenes and polysterenes, the physical properties change in about the same way with the average degree of polymerization. In this way the groups of hemicolloids and eucolloids show no sharp line of demarcation, but change gradually.

It should be noticed in this same table that in the series of polypranes only the first members of the eucolloids are known, *i. e.*, products with an average molecular weight of from 20,000 to 30,000. In hydrocarbons of this average molecular weight the characteristic properties of eucolloids occur, *i. e.*, the instability of the macromolecules in solution, the high viscosity of the solution and the strong swelling power do not appear very strongly since the sphere of action of the molecules is still not very great. Eucolloids with a very high average molecular weight, whose solutions show the properties characteristic of colloids, are known only in the series of polyprenes and polysterenes. Hydrorubbers of the same average

molecular weight as purified rubber, products of average molecular weight of from 80,000 to 100,000, have not been prepared up to now because the long rubber molecules are so sensitive that they are also partially decomposed by reduction in the cold.[43] Only with these very high molecular hydrorubbers should one expect the same properties as with rubber and polysterenes.

TABLE

HOMOLOGOUS POLYMERIC SERIES OF POLYPRANES, POLYPRENES, AND POLYSTERENES

Description	Hemicolloid	Eucolloid
Average molecular weight	1000–10,000	>10,000 to about 200,000
Average degree of polymerization	10–100	100–2000
Appearance of the products:		
Polypranes: (rubber and gutta-percha series)	Thin to thickly viscous sirup	Like purified rubber, however, much less tough and elastic
Polyprenes:		
(rubber series)	Greasy sirup	Tough and elastic
(gutta-percha series)	Powdery	Fibrous
Polysterenes	Powdery	Tough glass, elastic when warm
Solubility in benzene, carbon tetrachloride	Easily soluble without swelling	Slowly soluble with swelling
Solubility in acetone and alcohol	Insoluble	Insoluble
Behavior of a 5% solution in carbon tetrachloride	Slightly viscous	Highly viscous
Character of this solution	Sol solution	Gel solution
$\frac{\eta_{sp}}{c}$[44]	0.3–3	3–60
Hagen-Poiseuille Law	No deviations	The higher the molecular weight the greater the deviations

Elasticity of Hydrorubber

In the first communication on hydrorubber the opinion was expressed that the special elastic properties of rubber might be related to the unsaturated nature of the colloid molecule. This opinion was based on the observation that saturated highly polymeric substances, as for example, hydrorubber and polyvinyl bromide, are not elastic.[45] Also in the transformation of rubber into cyclorubber[46] by the action of concentrated sulfuric acid or zinc and hydrochloric acid on heating[47] the elasticity is lost. The cyclorubbers are powdery substances and are hemicolloidal in character.

Kirchhof[48] had previously expressed the opinion that the elasticity of rubber was related to the secondary valences of the double bonds. Recently Fikentscher and Mark[49] have come to a similar opinion, based likewise on the change in properties when rubber is transformed into hydrorubber.

According to more recent experience the elasticity of high molecular substances depends upon the length of their molecules. The hydrorubber obtained by Fritschi is a hemicolloid, as stated above, and it has, as do the hemicolloidal polyprenes and all other hemicolloids, no elastic properties. A hydrorubber of a molecular weight of about 30,000 is on the contrary solid and shows weak elastic properties, of course less than masticated rubber which has about the same average molecular weight. The saturated eucolloida[1] polysterene becomes elastic on heating;[50] in the cold it resembles to some extent frozen rubber. Therefore, the elasticity of rubber cannot

be ascribed to its double bonds. These compounds which are made up of fiber molecules are then elastic when the molecules are very long. Elasticity is a property of many macromolecular compounds. However, the presence of very long molecules is not sufficient to produce elastic properties; rather these properties probably depend upon the fact that in the elastic substances mixed homologous polymers are present,[51] without, however, it being necessary that every such mixture have elastic properties.

Solubility of Hydrorubber

Contradictory to the idea that in colloidal solutions of hydrorubber, as in those solutions of rubber itself, macromolecules are dissolved, and that the latter are responsible for the colloid properties, is the great solubility of these compounds. With a great many organic compounds, it has been found that with increasing molecular weight the solubility diminishes very much. Thus, in the series of paraffins, *e. g.*, di-myricyl with 60 carbon atoms in the chain is, for instance, very difficultly soluble, paraffins with 100 and more carbon atoms are soluble only with heating, and also only in a small amount.[52] Hydrorubbers with 100 to 1000 carbon atoms in the chain are, on the contrary, still easily soluble, and in rubber which has 5000 to 10,000 carbon atoms united in the long chain they still go into solution. Judged by the solubility of paraffins, this appears to be very improbable, and such considerations have already led to the theory of a special micellar structure for the colloidal particles of these products.

The solubility of organic compounds depends very greatly, however, on the form of the molecules. Moreover, relatively high molecular substances with branched chains are still readily soluble. The difference in solubility of normal paraffins and hydrorubbers depends upon the fact that in the former the molecules are symmetrically constructed, whereas the latter contain branched chains. Therefore, the intermolecular forces in normal paraffins are much stronger than in hydrorubbers, and to this is to be attributed the difference in solubility. Correspondingly, the normal paraffins as a result of the closer arrangement of the hydrocarbon chains have a higher specific gravity than hydrorubber.

Paraffin $C_{28}H_{72}$	$D = 0.942$[53]
Hydrorubber	$D = 0.858$–0.864

It often happens that with asymmetrical structure of the molecule the specific gravity decreases and solubility increases.

However, this does not explain an observation which was made at the beginning of this article and which is contradictory to the above points of view. Hydrobutadiene-rubber[54] has the same properties as hydrorubber. The product obtained at 270° is an amorphous, easily soluble sirupy mass. We expected to obtain as a reduction product of butadiene-rubber a solid crystallized, difficultly soluble paraffin. This contradiction was the greater as it was possible to convert polyvinyl haloids[55] and polyvinylacetate[56] into high molecular paraffins, and therefore to prove that substituted paraffin chains are present in these products. Hydrobutadiene-rubber is therefore not a high molecular paraffin. Its molecules are branched chains, which means that even synthetic butadiene-rubber itself has no normal molecular chains like natural rubber, but has a complex structure.

These various facts prevented our publishing our experiments, because it did not seem possible earlier to explain them in an incontrovertible manner.

References

[1] Part 24, *Helvetica Chim. Acta*, **13**, 1321 (1930).

[2] Published by Springer, **1919**, page 48.

[3] *Ber.*, **55**, 3458 (1922).

[4] *Helvetica Chim. Acta*, **5**, 785 (1922).

[5] Since the views on the structure of high molecular compounds are in a continuous state of flux among the individual investigators, we consider this advisable.

[6] *Helvetica Chim. Acta*, **5**, 800 (1922).

[7] Staudinger, *Ber.*, **62**, 2906 (1929); *Kolloid-Z.*, **51**, 71 (1930).

[8] Staudinger and Ashdown, *Ber.*, **63**, 717 (1930).

[9] See following communication.

[10] Staudinger, *Ber.*, **57**, 1203 (1924).

[11] In the phys. properties of the product, *e. g.*, in the toughness of solid hydrorubber, as in the viscosity of the solutions themselves, there are differences which will be dealt with later.

[12] Pummerer and Koch, *Ann.*, **438**, 303 (1924).

[13] Pummerer, Nielsen, and Gündel, *Ber.*, **60**, 2175 (1927)

[14] See Part 26 to follow.

[15] Huber, *Thesis*, Zürich, **1926**.

[16] Schaal, *Thesis*, Freiburg, i. Br., **1930**.

[17] Pummerer and Koch, *Ann.*, **438**, 294 (1924).

[18] Katz and Brag, *Z. angew. Chem.*, **38**, 439 (1925).

[19] Ott, *Naturwissenschaften*, **14**, 320 (1926).

[20] Staudinger, Johner, Signer, Mie, and Hengstenberg, *Z. phys. Chem.*, **126**, 435 (1927); Staudinger and Signer, *Ann.*, **474**, 169 (1929); *Ber.*, **62**, 2395 (1929).

[21] Staudinger, *Ber.*, **63**, 927 (1930).

[22] Staudinger and Signer, *Z. Krysi.*, **70**, 193 (1930).

[23] Staudinger and Bondy, *Ber.*, **63**, 724 (1930).

[24] See the articles by Pummerer and his co-workers.

[25] Staudinger, *Ber.*, **63**, 921 (1930).

[26] Unpublished experiments by Bondy.

[27] Decomposed rubber is much easier to purify since the molecules are shorter.

[28] See following work.

[29] Staudinger and Bondy, *Ann.*, **468**, 30 (1929); Staudinger, *Ber.*, **63**, 927 (1930); Staudinger, *Ibid.*, **63**, 927 (1930); Fikentscher and Mark, *Kautschuk*, **6**, 1 (1930).

[30] *Ber.*, **56**, 1050 (1923).

[31] Van Rossem, *Kolloidchem. Beihefte*, **10**, 83 (1918).

[32] The action of acids depends upon a cleavage of the macromolecules; Staudinger and Joseph, *Ber.*, **63**, 2888 (1930).

[33] Staudinger, *Ber.*, **63**, 921 (1930); *Kautschuk*, **6**, 153 (1930).

[34] Staudinger, *Ber.*, **57**, 1207 (1924).

[35] Probably differences in the stability exist. From experiments with the homologous polymeric polyprenes and with rubber, the high molecular compounds would have to be more easily cracked than the low molecular.

[36] Pummerer and Pahl, *Ber.*, **60**, 2159 (1927).

[37] For an understanding of the "Homologous polmyeric series," see Staudinger, *Z. angew. Chem.*, **42**, 69 (1929).

[38] Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

[39] Staudinger, *Ber.*, **59**, 3032 (1926) and later works.

[40] For sol solutions and gel solutions, see Staudinger, *Ber.*, **63**, 929 (1930); *Kautschuk*, **6**, 153 (1930).

[41] Staudinger and Machemer, *Ber.*, **62**, 2922 (1929); Staudinger, *Kolloid-Z.*, **51**, 87 (1930).

[42] Staudinger and Signer, *Ann.*, **474**, 180 (1930); Staudinger and Lüthy, *Helvetica Chim. Acta*, **8**, 41, 65 (1925).

[43] Unpublished experiments by Bondy.

[44] These values are calculated from η_{sp}-values 0.1–0.2, and, therefore, at such dilution that the Einstein law is still valid.

[45] Staudinger and Fritschi, *Helvetica Chim. Acta*, **5**, 789 (1922), Note 5.

[46] Staudinger and Widmer, *Ibid.*, **9**, 529 (1926).

[47] Staudinger and Geiger, *Ibid.*, **9**, 549 (1926).

[48] Kirchhof, *Kolloid-Z.*, **30**, 176 (1922); *Kautschuk*, **6**, 31 (1930).

[49] *Kautschuk*, **6**, 5 (1930).

[50] *Ber.*, **62**, 242 (1929).

[51] Staudinger and Machemer, *Ber.*, **62**, 2922 (1929); Staudinger, *Ibid.*, **63**, 929 (1930).

[53] Fischer and Tropsch, *Ber.*, **60**, 1330 (1927); Staudinger, Brunner, and Feisst, *Helvetica Chim. Acta*, **13**, 805 (1930).

[53] Hengstenberg, *Z. Kryst.*, **67**, 587 (1928).

[54] Staudinger, Brunner, and Feisst, *Helvetica Chim. Acta*, **13**, 805 (1930).

[55] From experiments by Schwalbach, see his *Thesis*, Freiburg i. Br., **1930**; Staudinger, *Kautschuk*, **5**, June (1929).

[56] *Thesis* by Brunner, Zürich, **1926**; *Helvetica Chim. Acta*, **13**, 805 (1930).

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Isoprene and Rubber

Part 26.[1] Hemicolloidal Hydrorubbers

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The reduction of rubber without solvent takes place only at 270°, according to experiments by Fritschi.[5] Below this temperature rubber is reduced only with difficulty and incompletely. In the dissolved condition, on the contrary, Pummerer and Burkard[6] showed that rubber can be reduced at ordinary temperature. In an earlier communication[7] it was accordingly assumed that on heating a cleavage of secondary colloid particles into primary ones (into macromolecules) takes place, and that heating, therefore, has about the same effect as strong dilution. A distinction was made between primary and secondary particles,[8] and it was assumed that the strong diminution in viscosity which is observed in dilute rubber solutions depends upon a cleavage of the secondary colloid particles, just as do the decreases in viscosity which rubber undergoes upon heating, and which have been generally described as depolymerization.

These earlier ideas of ours are, however, incorrect. An extensive cracking of the rubber molecules takes place upon heating, and this was more carefully investigated by Geiger[9] and later by Bondy.[10] In this way reduction is facilitated. With strong dilution, on the other hand, the rubber solution passes from the gel state to the sol state,[11] the rubber passes into normal solution, and therefore reduction can take place more easily in a dilute solution than in a concentrated one. With reduction by heat, therefore, a derivative of unchanged rubber cannot be expected; instead the hydrorubbers obtained, for example, those first prepared by Fritschi, are not reduction products of rubber itself, but are hemicolloidal decomposition products of the latter. Only by careful reduction in cold solution can one succeed in obtaining a hydrorubber in which the rubber molecules remain unchanged.[12]

That below 270° without solvent rubber is not reduced at all, or is reduced only with difficulty, indicates that in the solid product the long molecules lie parallel, and are therefore arranged to a certain degree rigidly. Solid rubber is therefore to be compared to a crystallized solid substance, although no lattice-like orientation of the individual atoms has yet taken place, rather than to a liquid in which the molecules are irregularly arranged.[13] As long as this parallel arrangement of the rubber molecules exists, no reduction occurs. Upon heating to 200° the rubber becomes liquid, because of a cracking of the macromolecules into hemicolloidal molecules, and these latter can be much more easily reduced.[14]

Course of Hydrogenation at 270°

If rubber is heated at 270° without solvent, it is decomposed to a great extent because of the instability of the rubber molecules. The cleavage fragments—hemicolloidal polyprenes of an average molecular weight of 2000–3000—are unstable and become cyclicized. Rubber is also changed to a hemicolloidal polycyclorubber by heating at 270°. This polycyclorubber is not completely saturated. Reduction with nickel at 270° transforms it into a saturated hydropolycyclorubber which from a chemical point of view behaves like a paraffin hydrocarbon. Accordingly, it is not attacked by concentrated nitric acid, in contrast to polycyclorubber. Such

an explanation[15] led to an understanding of the manifold phenomena which were observed in the reduction of rubber to hydrorubber at 270°. If this reduction proceeds rapidly, large quantities of a fairly active catalyst are used, *i. e.*, a nickel catalyst, and under these conditions the primary cleavage products formed from the rubber, the hemicolloidal polyprenes, will be immediately reduced without cyclicization. Only in this case can pure, homologous polymeric[16] hemicolloidal hydrorubbers be expected.

In order to judge the course of the reduction, it is furthermore very essential that *the molecules of the hydrorubber should be far more stable than those of rubber.* The rubber molecules, as has already been proved,[17] are very easily split up, because as a result of the adjacent double bonds the union between the two CH_2-groups is loosened greatly.

Since the union of the carbon atoms in the hydrorubber chain is stronger than in the rubber chain, a hydrorubber of a definite average molecular weight will be split up by heat only at a much higher temperature than a rubber of the same average molecular weight. Thus, for example, a 200-polyprane is not changed by a three-hour heating at 270°, while a 200-polyprene, as stated above, will be decomposed to approximately a 30-polyprene chain. If very rapidly reduced with large amounts of fairly active catalyst, relatively high molecular cleavage fragments of the rubber molecule will be transformed into the stable molecules of hydrorubber, since reduction proceeds more rapidly than cleavage. A product is, therefore, obtained of much higher viscosity than in a reduction with a poor catalyst. Since, however, the mixture of the catalyst with the solid rubber is never exactly the same, and since, furthermore, there are great differences among catalysts, hydrorubbers which are prepared under apparently the same conditions still show differences in behavior which are to be attributed to the differences in the molecular size. These are very readily proved by viscosity measurements. Thus with nickel as catalyst, hydrorubbers were obtained, the $\frac{\eta_{sp}}{c}$ values of which varied from 0.9 to 3. This corresponds to molecular weights of from 3000 to 10,000. On the other hand, in the slow reduction with less catalyst low molecular products were obtained, and this is the case if hydrogenation is carried out with a little platinum, according to Fritschi. These rubbers have $\frac{\eta_{sp}}{c}$ values of about 0.5 which corresponds to an average molecular weight of 1700.

Particularly favorable reducing conditions are to be had if rubber is first swollen, and if large quantities of nickel catalyst are dispersed in it in this condition, and it is then reduced. In this way Schaal obtained a product which had a $\frac{\eta_{sp}}{c}$ value of 5.0, corresponding to a molecular weight of about 17,000. In this swollen state the rubber molecules are greatly loosened, so that reduction can take place before they are cracked. It is remarkable that a hydrorubber of this high average molecular weight is stable a still longer time at 270°. There are accordingly even very large molecules which are capable of existing under relatively extreme conditions; such a study shows that at lower temperature macromolecules of entirely different dimensions can exist, that is, such dimensions as we ascribe to rubber,[18] with a molecular weight of 100,000 and more.

The great difference between the stability of the paraffin chains of hydrorubber and rubber itself is shown by the following experiment. If rubber is heated first at 270°, that is, is first decomposed and then reduced, the decomposition is much more extensive than if it is reduced simultaneously with cracking, and a hydropolycyclo-

rubber is obtained which has a molecular weight of only about 2300; therefore, it is a much lower molecular product than that obtained by reduction with cracking.

The following table shows again the differences in the various kinds of rubber according to the conditions of reduction. At the same time, it may also be judged to what extent decomposition of the rubber takes place during its reduction. The difference is especially evident if the $\frac{\eta_{sp}}{c}$ values are compared. Therefore, the viscosity of solutions of the various molecular colloids is measured in such a dilute state that the specific viscosity increases in proportion to the concn. (within the range of sol solutions). From the degree of dilution, the $\frac{\eta_{sp}}{c}$ values are obtained for a base molar solution, calculated on a C_5H_8 and C_5H_{10} group[19], respectively.

TABLE I

Product	$\frac{\eta_{sp}}{c}$	Average Molecular Weight	Degree of Polymerization
Crepe rubber	50–60	170,000	2500
Rubber purified by method of Pummerer	15–22	50,000–70,000	800–1000
Masticated rubber	7.6	27,000	400
Hydrorubber in solution reduced at 150° 200°	6–9	20,000–30,000	300–400
Hydrorubber in swollen state reduced at 270°	5.1	16,000	240
Hydrorubber at 270° from solid rubber, with much Ni	0.9–3	3000–10,000	45–140
Hydrorubber at 270° from solid rubber, with little Pt	0.5–1	1700–3000	25–45
Polycyclorubber	0.4[20]	2300[21]	34
Hydropolycyclorubber	0.36	2050	30

Abnormal Hydrogenation

According to experiments by Geiger,[21] as mentioned above, upon heating rubber a cyclicization of the hemicolloidal polyprene chains occurs, resulting in polycyclorubber. If rubber is reduced with little catalyst, therefore, under unfavorable conditions, as carried out above, a very extensive cleavage of the rubber takes place. However, a more or less strong cyclicization results, and this becomes greater the longer hydrogenation proceeds. A hydrorubber is obtained in this way which contains more or less cyclorubber groups. It could not be ascertained whether individual rubber molecules are strongly cyclicized and slightly reduced while others on the contrary are completely reduced, or whether the cyclo groups appear quite uniformly in the long fiber molecules. A separation of the product was not possible. This secondary reaction can be recognized by the saturated reduction products obtained which, however, have a higher carbon and lower hydrogen content than does hydrorubber.

Such cyclicizations also occur with hydrogenation in the cold. Pummerer and Koch[22] designate this type of hydrogenation which yields saturated compounds with greater carbon content as abnormal hydrogenations, and Pummerer and Nielsen[23] give the same explanation for it as that of Geiger for abnormal hydrogenation at higher temperatures.[24]

This abnormal hydrogenation can be much better proved by differences in refraction and in the density of the preparations than by elementary analyses. The specific gravity and refraction of hydropolycyclorubber are essentially higher than those of hydrorubber, just as polycyclorubber has a higher density and higher refractive power than rubber itself.[25]

Hydropolycyclorubber obtained by reduction of polycyclorubber also has other physical properties. Like cyclorubber, it is powdery, in contrast to hydrorubbers, which are sirupy. The following table shows that in rapid reduction with large quantities of catalyst, pure hydrorubber is obtained. Fritschi, because he used only a little platinum in the reduction, obtained weakly cyclicized hydrorubber. With copper as catalyst, on the contrary, a strongly cyclicized hydrorubber is obtained which has the appearance of a hydrocyclorubber obtained from reduction of a cyclorubber, because here the hydrogenation proceeds very slowly in comparison to the cyclization. This product is correspondingly very much decomposed.

TABLE II

DENSITY AND MOLECULAR REFRACTION OF RUBBER[26]

Product	Density	n_D^{16}	M_D Found for 1 Base Molecule	M_D Calculated for 1 Base Molecule
Rubber by method of Geiger	$d_4^{16} = 0.920$	1.5222	22.57	22.56
Rubber by method of Macallam & Whitby[27]	$d_4^{20} = 0.9237$	1.5219	22.46	22.56
Hydrorubber by method of Geiger reduced with Co	$d_4^{16} = 0.8585$	1.4768	23.06	23.01
Hydrorubber reduced with Ni	$d_4^{16} = 0.8610$	1.4770	23.00	23.01
Hydrorubber by method of Pummerer and Burkard	....	1.4755 1.4840	...	...
Hydrorubber by method of Fritschi, somewhat cyclicized	....	1.4820	...	...
Hydrorubber with copper oxide, considerably cyclicized	....	1.5130	...	...
Hydrocyclorubber, reduced cyclorubber, $C_{30}H_{34}$	$d_4^{16} = 0.968$	1.5263	...	...
Cyclorubber	$d_4^{17} = 0.992$	1.5387	21.48	...

Conclusions Regarding the Constitution of Rubber

The molecular refractions of rubber and of hydrorubber show that both are constituted like the corresponding low molecular compounds. Rubber possesses a double bond for every isoprene residue, which behaves like an ordinary double bond, as shown by the molecular refraction and numerous chemical reactions. If the double bonds of rubber are assumed to be engaged by micellar forces, and if, therefore, views like those expressed by Harries, Kirchhoff, Pummerer, Hoch, Meyer, Mark, and other investigators on the decomposition of colloidal particles of rubber, are considered, then this engagement of the double bonds would have to show itself in a change in the molecular refraction.

The hydrorubber obtained from rubber has the molecular refraction calculated for a saturated C_5H_{10} group, and therefore it has the value which is to be expected for a paraffin hydrocarbon. On the basis of these determinations and also on the basis of the fact that hydrorubber still has colloid properties, it is concluded that rubber has very high molecular weight. This conclusion depends upon the transformation of one molecular colloid into another.

Hemicolloidal Hydrogutta-Percha and Hydrobalata

By the same method, by which the homogeneous polymeric hydrorubbers had been obtained with Ni as catalyst at 270° under hydrogen pressure, gutta-percha and balata were also reduced, and products were obtained in that way which are identical in appearance and properties to hydrorubber.

	Density	n_c^{16}	Molecular Weight in Benzene
Hydrorubber	0.8585	1.4768	4500
Hydrogutta-percha	0.8595	1.4770	5300
Hydrobalata	....	1.4762	..

From these results it was concluded that rubber and gutta-percha must be distinguished as *cis-trans*-isomers, since, after the breaking up of the double bonds, the differences between the two products disappears.[28] Really they should be considered as diastereoisomeric hydroproducts, as shown in the previous work. Probably rearrangements occur at high temperature, so that the hydroproducts can no longer be distinguished.

Slight differences occur in the toughness of solid products and the viscosity of the solution with apparently the same reduction methods. Naturally, conclusions cannot be made on the differences in the constitution of the original substances, because, according to what has been said above, the products obtained at 270° from the original molecule by cleavage and the size of the cleavage fragments, and therefore the viscosity of the solution, change with the conditions of the experiment, and these conditions are never exactly the same. Thus it is difficult to carry out the reduction at exactly the same temperature in the rotating autoclave. It is of interest that reduction in the solid state of gutta-percha and balata yields much more highly decomposed products than when the reduction takes place in the swollen state; here therefore the same phenomena are observed as with rubber.

	Unreduced Product		Hydroproducts by Reduction of Solid Substance at 270° with Nickel		Hydroproducts by Reduction of Swollen Substance at 270° with Nickel	
	$\frac{\eta_{sp}}{c}$	Average Molecular Wt.	$\frac{\eta_{sp}}{c}$	Average Molecular Wt.	$\frac{\eta_{sp}}{c}$	Average Molecular Wt.
Rubber	20–50	70,000 to 200,000	1–3	3,000 to 10,000	5.1	16,000
Gutta-percha	25	80,000	1.64	5,500	4.2	14,000
Balata	15	50,000	..	...	6.7	22,000

EXPERIMENTAL PART

Technic of Hydrogenation of Rubber

The reduction of rubber was carried out in a Fierz rotary autoclave,[29] as in the first experiments by Staudinger and Fritschi, and 10 g. of crepe rubber purified by extraction with acetone were reduced at 270°–280°. In order to disperse the catalyst as finely as possible in the rubber, it was sprinkled into a highly viscous solution of rubber in benzene, then the rubber together with the catalyst was precipitated by the addition of alcohol and the mass dried *in vacuo*. The hydrorubber can be purified by solution in ether and precipitation with alcohol and acetone. Impurities which are still present in the not wholly purified rubber are separated in this way.[30] In the same way the catalyst is easily removed with these hemicolloidal products. The easy purification of this decomposition product depends upon the fact that rather concentrated solutions (3–5%) are still sol solutions, and therefore solutions in which the molecules are normally dissolved while the catalyst, like the impurities, is difficult to separate from the gel solution.

To determine the refraction, solutions of the samples were put into the Pulfrich refractometer, the solvent evaporated *in vacuo* and the residue dried to constant weight in high vacuo. The density determinations were carried out in a pycnometer; the preparation dried in a high vacuo was first warmed so that it became a thin liquid, and then was introduced into the pycnometer. The different experiments, summarized in Table III, gave the following results:

TABLE III

Catalyst Suspended in Rubber Rubber : catalyst	Catalyst	Temperature	Reduction Time in Hours	Initial Atmospheric Pressure[31]	Density[32] d_4^{16}	Refraction n_D^{16}
1:0.03	Pt black	275–280°	24	105	....	1.4840
1:0.5	Ni on pumice, 25% Ni	275–280°	2	100	....	1.4810
1:1	Ni on pumice, 25% Ni	275–280°	2	95	0.8638	1.4776
1:1	Ni on pumice, 25% Ni	275–280°	2	30	....	1.4814
1:1.5	Ni on pumice, 25% Ni	275–280°	10	100	0.8610	1.4770
1:1	Ni	275–280°	4	95	....	1.4804
1:1	Ni oxide-carbonate	275–280°	4	98	....	1.4822
1:1	Ni oxide-carbonate on pumice, 25%	275–280°	2	95	....	1.4805
1:1	Cobalt on pumice	275–280°	2	107	0.8585	1.4768
1:1	Cobalt oxide on pumice	275–280°	2	102	....	1.4805
1:1	Pyrophorous iron	275–285°	4	105	....	1.4792
1:1	Copper oxide on pumice, 25% CuO	275–285°	4	103	....	1.5130

In addition, a series of comparative experiments was made with platinum black and with the Ni catalyst prepared according to Kalbe.

TABLE IV

Rubber in g.	Catalyst in g.	Time in Hours	n_D^{61}
34	1.5 Pt	3	1.4833
33	1.6 Pt	3	1.4828
35	1.6 Pt	5	1.4825
30	2.5 Pt	4	1.4821
39	2.4 Pt	5	1.4823
13	13 Ni	2	1.4771
10	12 Ni	2	1.4770
12	12 Ni	2	1.4722

The experiments led to the following conclusions:

1. Cobalt and nickel are good catalysts, pyrophorous iron and platinum are poor ones. Copper reduces very little. The relatively poor reduction with platinum depends upon the fact that in this case little catalyst was used, and during the reduction it settled out, so that the greater part of the rubber did not come in contact with it. The product obtained with copper was essentially hydropolycyclorubber, as a comparison of the refraction exponents shows:

Hydropolycyclorubber $n_D^{16} = 1.5263$
Hydropolycyclorubber $n_D^{16} = 1.5130$

The physical properties of the product are more like those of cyclorubber than of hydrorubber. The product yields a solid substance which liquefies at 50° and gives solutions of low viscosity.

2. The catalysts precipitated on carriers[33] are more active than the metals themselves. Of the nickel catalysts prepared from nickel hydroxide, nickel cyanide, and nickel carbonate, that from nickel hydroxide proved to be the most active.

3. For a rapid hydrogenation, the amount of catalyst is of fundamental importance. With a ratio of 1:1 between catalyst and rubber, the maximum reducing power is already reached, as shown by the following refraction values:

	n_D^{16}
1 part rubber + 0.5 parts Ni catalyst	1.4810
1 part rubber + 1.0 parts Ni catalyst	1.4776
1 part rubber + 1.5 parts Ni catalyst	1.4770

Analyses of Hydrorubbers

1. The product reduced with cobalt which has the best refraction value was purified by repeated reprecipitations from ether-alcohol and ether-acetone and was analyzed. The hydrorubber is viscous, colorless, stable toward hot nitric acid and potassium permanganate, adds no bromine, and decomposes above 330°.

0.1856 g. substance gave 0.5825 g. CO_2 and 0.2380 g. H_2O
0.1623 g. substance gave 0.5091 g. CO_2 and 0.2091 g. H_2O
$C_{10}H_{20}$ calculated C 85.62 H 14.38%
found C 85.60; 85.55 H 14.35; 14.42%
$d_4^{15} = 0.8585$ $n_D^{15} = 1.4768$ M_D calculated 23.01, found 23.06
0.3210 g. substance 13.2 g. benzene $\Delta = 0.021°$, mol. wt. 4280
0.4290 g. substance 13.2 g. benzene $\Delta = 0.034°$, mol. wt. 4870

VISCOSITIES IN TETRALIN SOLUTION[34]
(DETERMINED IN THE OSTWALD VISCOSIMETER AT 20°)

Molarity (mol.)	η_r	$\frac{\eta_{sp}}{c}$	K_c	Molecular Weight Calc. from K_m[35]	Molecular Weight Calculated from K_3[36]
0.1	1.12	1.20	0.49	4000	4900
0.25	1.31	1.24	0.47		
0.5	1.72	1.44	0.47		

2. Highly viscous[37] hydrorubbers obtained with nickel

Found C 85.62 H 14.38%

0.1252 g. 17.4 g. benzene Δ = very slight mol. wt. above 10,000
0.1773 g. 17.4 g. benzene $\Delta = 0.002$ mol. wt. above 10,000
$n_D^{18} = 1.4772$ η_r in 0.5-mol benzene solution 2.5

$\frac{\eta_{sp}}{c} = 3.0$ Mol. wt. calculated from $\frac{\eta_{sp}}{cK_m} = 10{,}000$ ($K_m = 3 \times 10^{-4}$)

3. Low viscous[37] hydrorubber obtained with nickel

Found C 85.34 H 14.43%

0.0452 g. substance, 17.6 g. benzene, $\Delta = 0.005$, mol. wt. 2600
0.1962 g. substance, 17.6 g. benzene, $\Delta = 0.020$, mol. wt. 2850
$n_D^{18} = 1.4771$ η_r in 0.5-mol. benzene solution 1.46

$\frac{\eta_{sp}}{c} = 0.92$ mol. wt. calculated from $\frac{\eta_{sp}}{cK_m} = 3000$

4. Hydrorubber obtained with platinum as catalyst

Found C 85.62 H 14.45%

0.2240 g. substance, 17.6 g. benzene, $\Delta = 0.040$, mol. wt. 1620
0.1992 g. substance, 17.6 g. benzene, $\Delta = 0.036$, mol. wt. 1600
$n_D^{18} = 1.4821$ η_r in 0.5 mol. benzene solution 1.24

$\frac{\eta_{sp}}{c} = 0.48$ mol. wt. calculated from $\frac{\eta_{sp}}{cK_m} = 1600$

ADDITIONAL VISCOSITY MEASUREMENTS OF THE PRODUCTS BY FRITSCHI[38]
(PREPARED WITH Pt)

Raw Material	η_r in 0.5 Mol. Tetralin Soln.	$\frac{\eta_{sp}}{c}$	Mol. Wt. Calculated from $\frac{\eta_{sp}}{cK_m}$
Plantation rubber extracted with acetone	1.53	1.06	3000
Latex rubber extracted with acetone	1.26	0.52	1700
Synthetic rubber	1.26	0.52	1700

Hydrorubber from Swollen Rubber at 270°

(Experiments by H. Joseph and W. Schaal[39])

In these experiments rubber purified by the method of Pummerer was used which had, according to viscosity studies, an average molecular weight of about 70,000.[40] Large amounts of a very active nickel catalyst[41] were used for reduction, and 5 g. of rubber were intimately mixed with 2.5 g. of nickel catalyst, the rubber having been swollen in cyclohexane before the Ni-catalyst was added. The solvent was then partially removed *in vacuo*, so that the rubber was reduced in the swollen state. The reduction was carried out in a Fierz rotary autoclave for three hours at 270°, with steam under 55 atm. of hydrogen. The products so obtained were completely saturated with tetranitromethane. At 250° even under these more favorable conditions without solvent, no completely saturated product was obtained. The hydrorubber prepared in this way has very high molecular weight, because it was so quickly reduced that only a relatively slight cracking took place.

Analyses: Found C 85.62; 85.40; 85.47
H 14.09; 14.59; 14.25%

Molarity	η_r in CCl_4 Soln.	$\frac{\eta_{sp}}{c}$	Deviations from $\frac{\eta_{sp}}{c}$ of Original Value in %	K_c
1/32	1.16	5.12	..	2.1
1/16	1.31	4.96	..	1.9
1/8	1.62	4.96	..	1.7
1/4	2.77	7.08	35	1.8
1/2	6.03	10.06	95	1.6

As with other hemicolloids, the viscosity in very dilute solutions increased in proportion to the concentration. In concentrated solutions on the contrary there were deviations.[42]

From the lowest $\frac{\eta_{sp}}{c}$ values a molecular weight was calculated:

$$\frac{\eta_{sp}}{CK_m} = 16{,}000 (K_m = 3 \times 10^{-4}),$$

whereas out of the average of the K_c values according to the formula $K_c K_{cm}$ the value was $18{,}000 (K_{cm} = 10^4)$. It is very surprising that such a high molecular hydrorubber is still stable after heating three hours at 270°. Molecular weight determinations in cyclohexane solution according to the cryoscopic method were made on this product and also in camphor, according to the Rast method. The values varied greatly. A number of them were between 3000 and 6000, therefore, they did not agree with the viscosity measurements.[43]

Hydrogutta-Percha

1. Purification of gutta-percha.[44]

To purify the commercial gutta-percha it was dissolved in CCl_4 and the solution left standing in a separatory funnel until the insoluble very difficultly filterable foreign substances migrated to the surface. From the clear liquid below, the gutta-percha separated as a white, spongy mass of fibers by dropping the liquid into agitated alcohol.

0.1693 g. substance gave 0.5460 g. CO_2 and 0.1798 g. H_2O
0.1862 g. substance gave 0.6016 g. CO_2 and 0.1968 g. H_2O

$C_{10}H_{16}$ calculated C 88.15 H 11.85%
Found C 87.96, 88.12; H 11.89, 11.83%

Reduction of Gutta-Percha

The reduction was carried out like that of rubber. Nickel on pumice was used as catalyst, and for 10 g. of gutta-percha 10 g. of catalyst were used. The reduction commenced at 260°, and was so violent that the temperature rose to nearly 300°, while the pressure diminished at the same time. It was left for two hours at 270° and then allowed to cool. The reaction product was dissolved in ether, filtered off from the catalyst, and the hydrogutta-percha separated from the solution with alcohol. It is soluble in hydrocarbons, chloroform, carbon tetrachloride, and ether, and insoluble in acetone and alcohol. It was purified by precipitation from ether-acetone and ether-alcohol. It was a viscous colored liquid, which could not be distilled without decomposition, and which behaved like a saturated paraffin hydrocarbon toward hot nitric acid, potassium permanganate, and bromine in carbon disulfide.

0.1940 g. substance gave 0.6086 g. CO_2 and 0.2479 g. H_2O
0.2000 g. substance gave 0.6277 g. CO_2 and 0.2559 g. H_2O
$C_{10}H_{20}$ calculated C 85.62 H 14.38%
Found C 85.56, 85.60; H 14.30, 14.32%
$d_4^{16} = 0.8595$ $n_D^{16} = 1.4770$
0.3225 g. substance, 13.2 g. benzene, $\Delta = 0.024°$, mol. wt. 5300
0.2110 g. substance, 13.2 g. benzene, $\Delta = 0.015°$, mol. wt. 5400

VISCOSITY MEASUREMENTS IN THE OSTWALD VISCOSIMETER IN TETRALIN
(EXPERIMENTS BY A. SCHWALBACH)

Molarity	η_r	$\frac{\eta_{sp}}{c}$	K_c	Mol. Wt. Calculated from K_m	Mol. Wt. Calculated from K_c
0.25	1.41	1.64	0.60	5500	5900
0.5	1.94	1.88	0.58		

Another product gave the following values:

$n_D^{16} = 1.4780$ η_r in 0.5-mol. tetralin solution = 1.74

$\frac{\eta_{sp}}{c} = 1.5$ molecular weight from $\frac{\eta_{sp}}{cK_m} = 5000$

On the other hand, Joseph and Schaal had obtained a relatively little decomposed hydrogutta-percha in the reduction of gutta-percha in the swollen state in the presence of some cyclohexane with a large excess of very active nickel as catalyst, as in the case of rubber.

VISCOSITY OF CCl_4 SOLUTIONS IN OSTWALD VISCOSIMETER

Molarity	η_r	$\frac{\eta_{sp}}{c}$	Deviations from $\frac{\eta_{sp}}{c}$ of Original Value in %	K_c
0.125	1.53	4.24	..	1.5
0.25	2.36	5.44	28	1.5
0.5	4.57	7.14	68	1.3

Molecular weight from $\frac{\eta_{sp}}{cK_m} = 14{,}000$

Molecular weight from $K_m K_{cm} = 14{,}500$
Molecular weight of the gutta-percha = about 30,000

Hydrobalata

Balata was prepared like gutta-percha from the commercial material.

It was not different from gutta-percha and according to our investigations both hydrocarbons are identical.[45] Both are fibrous, crystallized products. The reduction of balata proceeded like that of gutta-percha, and the hydroproducts have the same appearance and behavior:

0.1564 g. substance gave 0.4906 g. CO_2 and 0.2029 g. H_2O

(C_5H_{10}) calculated C 85.62%; H 14.38%
Found C 85.55%; H 14.52%
$n_D^{16} = 1.4762$

The solutions of this hydrobalata have low viscosity.

With a large excess of very active nickel catalyst (5 g. balata, 12.5 g. catalyst) Schaal obtained from balata in the swollen state in the presence of cyclohexane a hydrobalata which gave solutions of high viscosity and which therefore has a high molecular weight.

VISCOSITY OF CCl_4 SOLUTIONS IN THE OSTWALD VISCOSIMETER

Molarity	η_r	$\frac{\eta_{sp}}{c}$	Deviations from $\frac{\eta_{sp}}{c}$ of Original Value in %	K_c
0.125	1.84	6.7	...	2.1
0.25	3.35	9.4	40	2.1
0.5	8.17	14.3	113	1.8

Molecular weight from $\frac{\eta_{sp}}{cK_m} = 22{,}000$

Molecular weight from $K_cK_{cm} = 20{,}000$
Molecular weight of balata = about 50,000[46]

References

[1] Part 25 preceding.

[2] *Thesis*, Geiger, Zürich, **1926.** The results of this work have already been referred to in summary fashion in *Kautschuk*, **1**, 9 (1925). Since the journal of that year was not widely distributed and is now out of print, this subject will be reported again. The opportunity will be taken to correct a few ideas which have been changed by the work of the last five years.

[3] Huber, *Thesis*, Zürich, **1926.**

[4] Schall, *Thesis*, Freiburg i. Br., **1930.**

[5] Staudinger and Fritschi, *Helvetica Chim. Acta*, **5**, 785 (1922); Fritschi, *"Die Konstitution des Kautschuks und das Wesen der Vulkanisation,"* Seldwyla-Verlag, Zürich, **1923.**

[6] Pummerer and Burkard, *Ber.*, **55**, 3458 (1922).

[7] Staudinger, *Ber.*, **57**, 1207, Note 11 (1924).

[8] See in this connection the later concept on micelles of Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

[9] Staudinger and Geiger, *Helvetica Chim. Acta*, **9**, 549 (1926).

[10] Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

[11] Staudinger, *Ber.*, **63**, 929 (1930); Staudinger, *Kautschuk*, **6**, 153 (1930).

[12] See Part 29 (later) by Staudinger and Feisst.

[13] Staudinger, *Ber.*, **62**, 2901 (1929).

[14] With longer heating at 150°–200°, with the exclusion of oxygen, the rubber becomes insoluble. Here probably a linking of the individual, parallelly arranged fibers takes place, with formation of three-dimensional molecules, a process which may be compared to vulcanization. This insoluble product cracked upon heating at 270° and is transformed into soluble fragments so that the product of the cracking at 270° may also contain decomposition products of such three-dimensional molecules. Since hydrogenation at 270° takes place very rapidly, this secondary reaction is of little significance and may be disregarded.

[15] Staudinger and Geiger, *Helvetica Chim. Acta*, **9**, 549 (1926).

[16] For the idea of polymeric homogeneity see Staudinger, *Ann.*, **474**, 154 (1929).

[17] Staudinger, *Ber.*, **57**, 1203 (1924); Staudinger and Rheiner, *Helvetica Chim. Acta*, **7**, 25 (1923).

[18] Such experiments on the stability of paraffin hydrocarbons may be of further interest in the preparation of highly viscous, *i. e.*, high molecular lubricating oils. See also the later work.

[19] Staudinger, *Kolloid-Z.*, **51**, 71 (1930).

[20] Accordingly, $K_m = \frac{\eta_{sp}}{c} = 1.7$; in cyclorubbers K_m is smaller than in the polyprene series where $K_m = 3 \times 10^{-4}$; see *Kautschuk* **6**, 155 (1930).

[21] Staudinger and Geiger, *Helvetica Chim. Acta*, **9**, 554 (1926).

[22] Pummerer and Koch, *Ann.*, **438**, 310 (1924).

[23] Pummerer and Nielsen, *Ber.*, **60**, 2171 (1927); *Handbuch der Kautschuk-Wissenschaften*, page 256.

[24] Geiger, *Thesis*, Zürich, **1926**; Staudinger, *Kautschuk*, **1**, 9 (1925).

[25] Staudinger and Geiger, *Helvetica Chim. Acta*, **9**, 555 (1926).

[26] *Kautschuk*, **1**, 9 (1925).

[27] Maccallam and Whitby, *Trans. Roy. Soc. Canada*, **19**, III, 191 (1924).

[28] Staudinger and Bondy, *Ann.*, **468**, 30 (1929).

[29] H. E. Fierz, *Farbenchemie*, 2nd Ed., Verlag Springer, Berlin, **1922**, illustration 37, page 215.

[30] Hemicolloidal hydrorubber can be purified much better than macromolecular rubber; see preceding work.

[31] The final pressure is around 10 atm. less than the initial pressure.

[32] On account of the difficult determination, it was determined in only a few cases.

[33] For the preparation of nickel catalysts see Kelber, *Ber.*, **49**, 55 (1916); *Ber.*, **57**, 142 (1924); Lietz, *J. prakt. Chem.*, [2], **108**, 52 (1924); Normann, *Ber.*, **55**, 2193 (1922); Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 132 (1921).

[34] The viscosity of this product was determined later by Schwalbach.

[35] See the summary of the following work.

[36] *Ber.*, **63**, 921 (1930).

[37] The viscosity and also the size of the molecules of hydrorubbers vary very greatly in apparently the same preparation. The above data refer to two hydrorubbers which deviate very much from one another. The molecular weight determination is not precise, since the viscosity was measured in too concentrated a solution. Probably some solvent was still present in the preparation of product (2), so that the swollen rubber was reduced.

[38] Staudinger and Fritschi, *Helvetica Chim. Acta*, **5**, 785 (1922); Fritschi, *Die Konstitution des Kautschuks*, Verlag Seldwyla, Zürich, **1923**.

[39] Schaal, *Thesis*, Freiburg, i. Br., **1930**.

[40] Staudinger, *Ber.*, **63**, 921 (1930).

[41] This nickel catalyst was prepared by the reduction of nickel oxide according to directions by Hückel

[42] Staudinger, *Kolloid-Z.*, **51**, 71 (1930).

[43] See the following work. It may be possible that because of the great excess of highly active catalysts a normal hydrorubber results.

[44] Staudinger and Bondy, *Ber.*, **63**, 724 (1930), the purification of balata.

[45] Staudinger, *Ber.*, **63**, 927 (1930).

[46] Staudinger and Bondy, *Ber.*, **63**, 736 (1930).

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Isoprene and Rubber

Part 27.[1] The Relations between Viscosity and Molecular Weight of Hydrorubbers

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As has been shown in an earlier work,[2] in solutions of like concentration of homologous paraffins, the increase in the specific viscosity—the increase in the viscosity of the solvent by the dissolved substance—is proportional to the length of the molecules. This is the simplest case where proof could be found for this fact which is so important in explaining the constitution of molecular colloids, and where it was possible to show[3] the validity of the law: $\frac{\eta_{sp}}{cM} = K_m$

The hydrorubbers, the polypranes, represent a series of homologous paraffin hydrocarbons. They appear to be particularly adapted for following the above conformity to law to a still further point, for here in distinction to simple paraffins, even the high molecular members are still solids.

On the basis of material already at hand,[4] an idea of the size of constant K_m could be obtained in this series. In the case of paraffins with normal chains, this constant was determined to 1.1×10^{-4} for a base molar solution, and, therefore, for a solution which contains one CH_2-group (14 g.) in solution. Calculated on the CH_2—CH_2—CH_2CH_2-group as it occurs in hydrorubber, the constant $K_m = 4.4 \times 10^{-4}$, if the unknown effect of the side CH_3-group is disregarded. With hemicolloidal polyprenes, the constant K_m for a base molecule C_5H_8 was found[5] to be 3×10^{-4}.

Finally in the decomposition products of hydrorubber the value 3.5×10^{-4} was obtained, and it, therefore, had the same order of magnitude.[6] That the constant K_m cannot be essentially different in the series of hydrorubbers from that in the series of polyprenes may be seen by the fact that in the reduction of hemicolloidal polysterenes[7] and polyindenes[8] neither the molecular weight nor the viscosity of the solution changes. Therefore, in the hexahydropolysterene and hexahydropolyindene series there must be approximately the same relations between viscosity and molecular weight as in the case of the polysterene and polyindene series.

For hydrorubbers, therefore, constant K_m would be expected to have the value from 3×10^{-4} to 4×10^{-4}.

Investigation of Technical Hydrorubbers

In the first experiments hydrorubbers prepared by reduction at various temperatures were used. A very extensively decomposed product was obtained by reduction at 320°–350° which had the character of a lubricating oil.[9] At lower temperature, *viz.*, 250°–300°, the products were thicker, more viscous but still hemicolloidal in character.[10] The molecular weight of a few of these products was determined by the osmotic method in benzene, besides which the viscosity was determined in the Ostwald viscosimeter. The molecular weight was then calculated from the

viscosity measurements, in one case from the $\frac{\eta_{sp}}{c}$ values at the lowest concentration by means of the constant $K_m = 3 \times 10^{-4}$, and in another way from the constant K_c in the following formula:

$$M = K_c K_{cm} \left(K_c = \frac{log\ \eta_r}{c} \right)$$

by which the same value for K_{cm} was obtained as for polyprenes, about 10^4. The $\frac{\eta_{sp}}{c}$ values were then used in order to calculate the constant K_m by means of the molecular weight found according to the cryoscopic determinations in benzene.[11]

TABLE I

Technical Hydrorubbers Obtained with Ni-catalyst	Mol. Wt. Found in Benzene	$\frac{\eta_{sp}}{c}$	K_m Estimated 3×10^{-4}	K_c	Mol. Wt. Calculated from $\frac{\eta_{sp}}{cK_m}$	Mol. Wt. Calculated from $K_c K_{cm}$
Viscous oil, prepared at 300°–340°	600	0.46	7.5×10^{-4}	0.19	1500	1900
Thick oil, prepared at 280°–300°	1350	1.74	13×10^{-4}	0.60	5800	6000
Solid, sticky product prepared in concentrated tetralin solution at 240°–245°	2450	4.8	20×10^{-4}	1.38	16,000	14,000

According to the foregoing measurements there is the same relation between viscosity and molecular weight in the hemicolloidal hydrorubber series as with the other hemicolloids;[12] here too the more viscous products have a higher molecular weight. However, constant K_m deviates sharply from the value 3×10^{-4} estimated above. It is much greater and decreases very sharply. With these products there is not the conformity to law which has been found for a larger series of other hemicolloids.[13]

Investigation of Pure Hydrorubbers

The molecular weight and viscosity were determined by Geiger and Huber for a few hydrorubbers prepared by rapid reduction on a small scale. These values showed that the same relation between viscosity and molecular weight holds true with these polypranes, prepared under more favorable conditions, as with the polyprenes. The mean value of constant K_m for four different determinations is 3.0×10^{-4}. It, therefore, has the same magnitude as had been found previously with hemicolloidal polyprenes. Likewise, the constant K_{cm} is of the order of magnitude of about 10,[4] and it is therefore the same as that of the polyprene series, for if the molecular weight is calculated by means of this constant from the K_c values, it is about the same as that determined by the cryoscopic method.

Since constant K_m in the polyprane series has the same value as in the polyprene series, the interesting result is obtained that the length of the molecule plays an essential part in the viscosity of the solution of homopolar molecular colloids. Differences in the structure of the molecules, which are very important in the chemical behavior of ethylene spaces in the chain, are not distinguishable. According to earlier ideas,[14] it might have been expected that the unsaturated polyprene chains are more highly solvated than the saturated polyprane chains, and that substances of the same average molecular weight in the polyprene and polyprane series would give solutions of different viscosity. Since this is not the case the earlier ideas on the solvation of homopolar colloidal molecules are incorrect.

They have no solvate layer of increasing magnitude; instead the solvate layer is monomolecular and is approximately the same for all homopolar colloidal molecules.[15] The viscosity of solutions of molecular colloids does not depend, as was generally assumed previously, upon the solvation of the molecules or micelles,[16] but depends only upon the length of the molecules.

TABLE II

Prepared by	Product	Molecular Weight Determined in Benzene	$\frac{\eta_{sp}}{c}$	K_m	K_c	Mol. Wt. Calculated from $\frac{\eta_{sp}}{K_{cm}}$ $K=3\times10^{-4}$	Mol. Wt. Calculated from K_cK_{cm}
Geiger	Hydrorubber	4550	1.2	2.6×10^{-4}	0.48	4000	4800
Geiger	Hydrogutta-percha	5360	1.64	3.0×10^{-4}	0.59	5500	5900
Huber	Hydrorubber	2700	0.92	3.4×10^{-4}	0.33	3000	3300
Huber	Hydrorubber	1600	0.48	3.0×10^{-4}	0.19	1600	1900

In addition, Stirnemann[17] carried out a larger series of experiments with hydrorubbers in order to find relations between viscosity and molecular weight, and he came to the conclusion that solutions of equal viscosity may have a different average molecular weight. This has already been referred to, and the following explanation given for this observation.[18] With mixtures of homologous polymers, such as are present in all cases, the molecular weight influences the lower member very greatly, and the viscosity of the solution influences the higher molecular members in particular, so that according to the composition mixtures may result which show quite different viscosities with the same average molecular weight.

In preparing hydrorubbers favorable results are to be expected[19] only when very large amounts of catalyst are used, when the reaction therefore proceeds rapidly and uniformly. This is not the case with the technical products prepared in the majority of cases with but little catalyst.

An undisputable explanation for the great deviations of constant K_m in commercial hydrorubbers is not yet available. However, the following facts should be taken into consideration. Nodzu observed that in molecular weight determinations of many high molecular hydrorubbers, gelatinous deposits are formed upon cooling, and these may be easily overlooked. Therefore, molecular weight determinations are deceptive.[20]

According to the experiments by Nodzu, irregularities likewise occur in boiling benzene. Thus the boiling point rises upon the introduction of a small quantity of hydrorubber and then decreases upon further additions, without there being any explanation.[21] The molecular weight therefore cannot be determined according to the ebullioscopic method.

However, we consider that the chief reason for the discrepancies is that the technical products which were prepared under unfavorable conditions of reduction are not representative of the homologous polymeric series of polypranes. In the case of products produced on a somewhat greater scale the reduction took place with relatively little catalyst and considerable secondary reactions occurred. Thus on the one hand, cyclicizations take place, as in the previous work, then again because of the longer heating in the autoclave, there may also be an initial linking of the individual fiber molecules which leads to a formation of three-dimensional molecules.[22] The products of the cracking are then no longer fiber molecules, but are very complex. They are paraffin hydrocarbons with branched chains.

Thus with homologous polymeric hydrorubbers, which we at first considered particularly suitable for studying the relations between viscosity and molecular weight, it is especially difficult to establish any conformity to law on account of the difficulty of preparing pure, and therefore homogeneous polymeric products.

Homologous polymeric polysterenes prepared in the cold are far better suited[23] to this purpose.

References

[1] Part 26, preceding.

[2] Staudinger and Nodzu, *Ber.*, **63**, 721 (1930).

[3] Staudinger and Heuer, *Ber.*, **63**, 222 (1930).

[4] Staudinger, *Kolloid-Z.*, **51**, 71 (1930).

[5] Staudinger and Bondy, *Ber.*, **63**, 734 (1930).

[6] See Part 28 later.

[7] Staudinger and Wiedersheim, *Ber.*, **62**, 2406 (1929).

[8] Staudinger, Johner, Schiemann, and Wiedersheim, *Helvetica Chim. Acta*, **12**, 962 (1929).

[9] Experiments were undertaken to obtain such products as very thick lubricating oil, and it was expected that there would be the advantage that such products, which have not yet found application technically any more than the more viscous hydrorubbers, would be extraordinarily stable.

[10] The Gesellschaft für chemische Industrie in Basel has kindly put at our disposal the above samples of hydrorubber. For this we wish to thank the management of the firm.

[11] Staudinger, *Kolloid.-Z.*, **51**, 71 (1930).

[12] Staudinger, *Ber.*, **59**, 3031 (1929).

[13] Staudinger, *Kolloid.-Z.*, **51**, 71 (1930).

[14] See especially Fikentscher and Mark, *Kolloid.-Z.*, **49**, 142 (1929).

[15] Staudinger and Heuer, *Ber.*, **62**, 2933 (1929); *Ber.*, **63**, 222 (1930).

[16] Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

[17] Unpublished experiments by Stirnemann (1925).

[18] *Helvetica Chim. Acta*, **12**, 942 (1929).

[19] *Ann.*, **438**, 308 (1924).

[20] The preparation of high molecular hydrorubbers depends upon their low solubility. As it appears, pure hydrorubbers are much more easily soluble than the abnormal hydrogenation products. Pummerer, Andriessen, and Gündel, *Ber.*, **62**, 2628 (1928) have recently made observations on the discrepancies in molecular weight determinations. These depend, however, upon the fact that the measurements were made in the region of gel solution. See Part 23 on Isoprene and Rubber, *Ber.*, **63**, 2900 (1930).

[21] The surface tension of hydrorubber solutions as observed by Bondy is different from that of a rubber solution.

[22] The linkage of the fiber molecules to form insoluble products takes place when rubber is heated cautiously. See Note 6 of the preceding article.

[23] Staudinger and Heuer, *Ber.*, **63**, 222 (1930).

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[Contribution from the Chemistry Department at The Ohio State University]

NATURAL AND SYNTHETIC RUBBER. VII. FRACTIONAL PRECIPITATION OF NATURAL RUBBER

By Thomas Midgley, Jr., Albert L. Henne and Mary W. Renoll

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Crude rubber is an indeterminate mixture of several substances. The constituents of the mixture can be classified as "resins," soluble in acetone, rubber hydrocarbon $(C_5H_8)n$, soluble in benzene and insoluble "proteins."

The so-called "resins" are conveniently removed by a Soxhlet extraction with acetone. This treatment leaves behind a mixture of the rubber hydrocarbons and the "proteins." The latter can be separated by a variety of methods, which are well summarized by Fisher.[1] However, none is entirely satisfactory, because the methods based on a physical property effect only an imperfect separation, while chemical methods injure one or both constituents.

This paper presents a method of separation based on the progressive precipitation of natural rubber from a mixture of alcohol and benzene by slow cooling. Within certain limits, a system containing definite amounts of natural rubber, benzene and alcohol is homogeneous above a definite temperature, its critical temperature of solution. This critical point is best determined by allowing a hot mixture of rubber, alcohol and benzene to cool and reading the temperature at which a sudden increase of turbidity occurs. The determination can be duplicated within 0.3°.

When a mixture of rubber, alcohol and benzene is heated to a temperature higher than its critical point, until it has become completely clear, and is then allowed to cool to a temperature about 1° below its critical point, a certain amount of gel collects at the bottom of the container, while the supernatant liquid becomes transparent. The gel is a mixture of rubber and nearly all of the "protein." The supernatant liquid contains rubber practically free of "protein"; it can be decanted and yields its rubber content upon cooling or by alcohol addition. If a very pure hydrocarbon is desired, the procedure is repeated.

To systematize the preparation of nitrogen-free rubber, the diagrams given in Figs. 1, 2 and 3 have been experimentally determined. The procedure used was the customary one for the determination of critical temperatures of solution. Figure 1 refers to crude crepe rubber, alcohol and benzene; Fig. 2 refers to pure rubber hydrocarbon, alcohol and benzene; and Fig. 3 refers to synthetic rubber (sodium rubber), alcohol and benzene. The diagrams show that the isotherms have generally the same trend; they are located farther to the right in Fig. 3 than in Fig. 2, and in Fig. 2 than in Fig. 1.

[1] H. L. Fisher, *Chem. Reviews*, **7**, 51 (1930); *J. Chem. Education*, **8**, 7 (1931).

The use of the diagrams is almost self-evident. A system containing 2.0% of natural rubber, 23.1% of alcohol and 74.9% of benzene is found to have a critical temperature of 43.0°. Such a system is represented by the circle *A* on Fig. 1. When this system is kept at 43.0°, it separates into two phases. The gel phase precipitates; it is a mixture of rubber hydrocarbon, "protein" and solvent, with a ratio benzene–alcohol larger than that of the system taken as a whole. The supernatant liquid contains

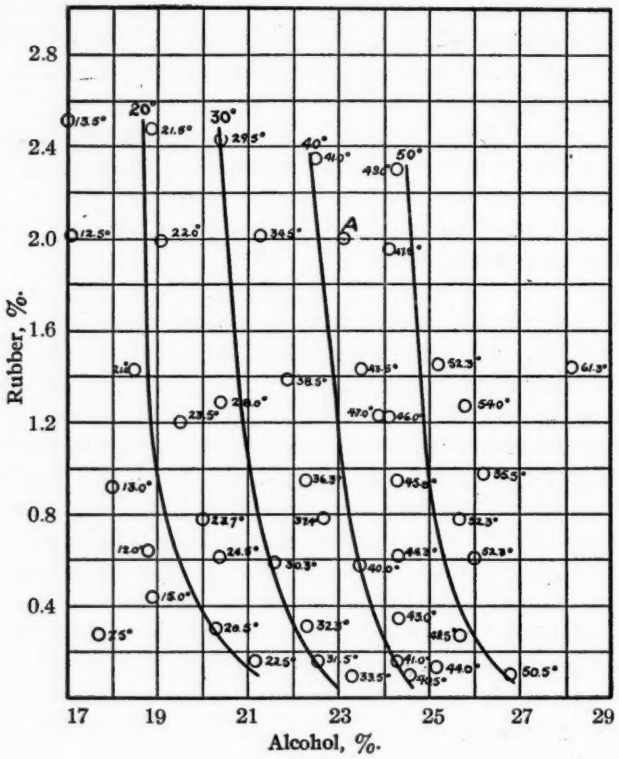

Fig. 1.

rubber practically free of nitrogenous matter, dissolved in benzene–alcohol, and in this liquid the ratio benzene–alcohol is smaller than in the system taken as a whole. The composition of the supernatant liquid is represented by the circle B, on Fig. 2; it corresponds to 0.55% of nitrogen-free rubber, 30.7% of alcohol and 68.75% of benzene. When such a system is cooled to 41°, it becomes heterogeneous and when it is cooled to 35°, it retains less than 0.1% of dissolved rubber.

Experimental Procedure

Two hundred and fifty grams of crepe rubber with a nitrogen content of 0.25% was dissolved in 8083 g. of benzene, heated to about 50°. A hot mixture of 4500 cc. of

absolute alcohol and 1400 cc. of benzene was added slowly, with constant stirring, until complete solution was obtained. The critical temperature, determined on a 50-cc. sample, was 43.0°. The mixture was then held at 42.0° in a thermostat, for one hour. At the end of this period, the mixture was no longer homogeneous, but consisted of a completely settled gel phase and a clear supernatant liquid. This liquid was decanted, then cooled in an ice-bath, and yielded 52.9 g. of rubber hydrocarbon, hereafter designated as A_1. After removal of the A_1 rubber, the liquid was warmed and poured back on the gel phase. By warming and stirring, the gel phase was caused to dissolve, and a clear solution was then obtained. A sample of this solution exhibited a critical point of 43.5°. Consequently, the solution was placed in a thermostat regulated at 42.5° for one hour, and the above procedure was repeated. This time 30.5 g. of rubber hydrocarbon was obtained, called A_2 hereafter. Two repetitions of these operations yielded fractions A_3 and A_4.

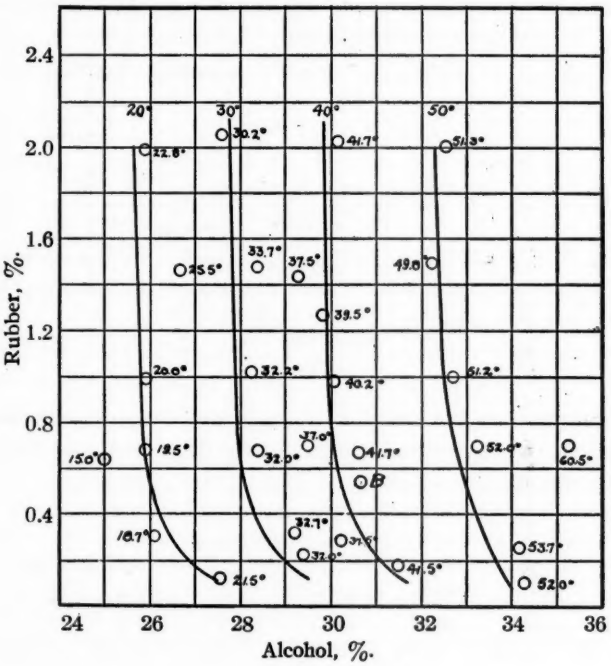

Fig. 2.

After the fraction A_4 had been collected, it was found that the gel phase would no longer dissolve completely in the alcohol–benzene mixture, even when the solvent was brought to its boiling point. Consequently, the insoluble matter was separated from the solvent; the solvent, upon cooling, yielded a fraction called A_5. Finally, the insoluble matter was extracted in a Soxhlet extractor with benzene. The material obtained from the benzene was called A_6, while the insoluble matter was called B. The various fractions were then analyzed for nitrogen. They were decomposed according to the usual Kjeldahl procedure.[2] After the addition of alkali, three 50 cc. portions were

[2] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1927, Vol. II, p. 1593.

distilled, nesslerized, and compared with a set of standard tubes. Blanks were run on all reagents; ammonia-free water was used throughout. Fraction B was decomposed by the usual Kjeldahl method, but the distillate was received in standardized hydrochloric acid, whose excess was titrated with standard sodium hydroxide.

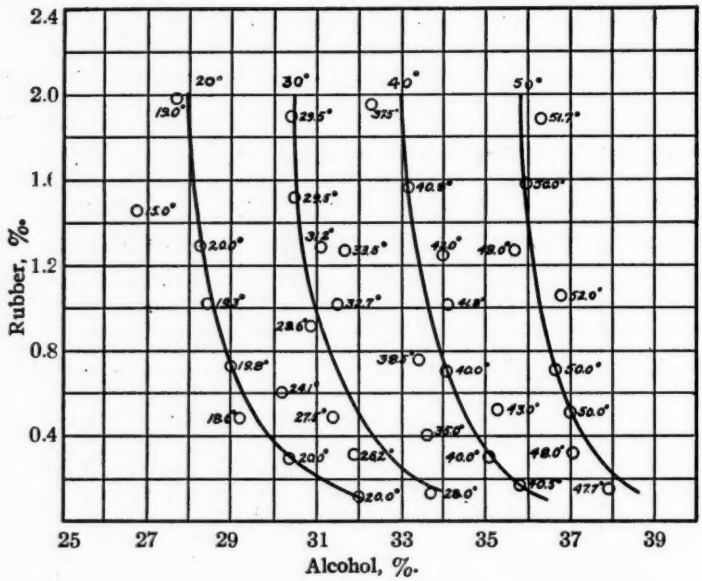

Fig. 3.

Table I summarizes the amounts of each fraction obtained, their critical temperature in the mixture alcohol–benzene described, and their nitrogen contents, by weight.

TABLE I

FIRST FRACTIONATION

	A_1	A_2	A_3	A_4	A_5	A_6	B
Grams	52.9	30.5	26.6	23.6	24.8	38.9	11.6
Crit. temp.	43.0	43.5	44.0	44.7	45.5	....	...
Nitrogen, %	0.026	0.033	0.044	0.125	0.142	0.160	4.21

After the first fractionation was completed, fractions A_1, A_2 and A_3 were combined, dissolved in a mixture of alcohol–benzene, and the whole procedure was repeated. Five successive fractions were thus obtained, as during the first fractionation, and they were analyzed for nitrogen. The results are reported in Table II.

TABLE II

SECOND FRACTIONATION

	A_{1-2}-1	A_{1-2}-2	A_{1-2}-3	A_{1-2}-4	A_{1-2}-5
Grams	28.1	17.1	13.8	16.0	6.4
Nitrogen, %	0.000	0.021	0.028	0.048	0.100

Fractions A_2–2, A_2–3 and A_2–4 were combined, dissolved in alcohol–benzene, and refractioned as previously. The results were as shown in Table III.

TABLE III

THIRD FRACTIONATION[3]

	A_3–1[a]	A_3–2	A_3–3
Grams	20.8	6.1	7.8
Nitrogen, %	0.000	0.011	0.015

[a] The carbon and hydrogen contents of Fraction A_3–1 were determined by microcombustion. Calcd.: C, 88.17; H, 11.83. Found: C, 88.28, 88.32; H, 11.74, 11.74. This indicates the complete absence of oxygen.

The rubber hydrocarbon obtained by cooling the supernatant liquid has, so far, been referred to as "nitrogen-free rubber." When freshly prepared, this material bears a strong resemblance to the so-called "α-rubber" of Pummerer[4] and it probably contains little if any "β-rubber." During the course of the fractionation, the "β-rubber" seems to concentrate in the fractions rich in protein.

Summary

Temperature–concentration diagrams are given of the systems natural rubber–alcohol–benzene, pure rubber–alcohol–benzene and synthetic rubber–alcohol–benzene. A method based on these diagrams is given for the separation of nitrogen-free rubber hydrocarbon by fractional precipitation of natural rubber from a mixture of alcohol and benzene.

COLUMBUS, OHIO

[3] A point of interest in the behavior of the rubber hydrocarbon was discovered in the course of this fractionation. For example when A_3–2 was dissolved in benzene and precipitated with acetone, only 14.1 g. was recovered. The other 3 g. remained in the turbid solution, irrespective of the amount of acetone added. The addition of water, however, caused precipitation. Likewise, the addition of a small amount of acetic acid would cause precipitation, seemingly at a different P_H. The residual three grams recovered by the addition of water was nitrogen-free.

[4] H. L. Fisher, *Chem. Reviews*, **7**, 65 (1930).

Reprinted from Analytical Edition, Industrial and Engineering Chemistry, Vol. 3, No. 3, page 297. July 15, 1931.]

Scorching, and Other Plasticity Changes in Rubber Compounds on Heating[1]

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A method is described which employs the Goodrich plastometer for detecting the initial stages of vulcanization of uncured rubber compounds. Reduction in plasticity, at standard room temperature, of test pieces previously heated for various intervals at selected temperatures is used to determine the degree of cure and thus to estimate safe operating temperatures and periods. Examples of the application of the method to a variety of compounds are presented. Other temperature effects, such as heat stiffening and softening, which have not previously been reported, are illustrated.

IN THE study of the temperature coefficient of plasticity of compounded rubber stocks with the Goodrich plastometer (*1*), it was observed that frequently an abrupt drop in plasticity values occurred at temperatures surprisingly low as compared with those of factory cures. This suggested that the instrument might easily be adapted to the estimation of the scorching tendencies of different compounds. This note will describe the methods adopted for demonstrating the changes in plasticity which take place at temperatures corresponding to those of mixing mills and calenders. Since it is intended only as a description of experimental methods the general nature only of the stocks used in illustration will be given; detailed reports of the behavior of accelerators, retarders, etc., are planned for future publication.

[1] Received April 7, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

The literature on rubber contains frequent references to methods of measuring relative scorching of accelerated mixes. This has been reviewed by Thies (*3*) who proposed that the relative solubilities of compounds at the end of various periods be used as an index of the degree of cure and thus afford a means of comparing the activities of accelerators. It does not appear that this method has any advantages in economy of time and material over plastometric measurements such as used by Krall (*2*) and adopted by several laboratories, nor does it afford the exactness possible with the latter method. As pointed out by other observers (*4*), the Williams plastometer is less sensitive than the Goodrich instrument, so we might expect the latter to bring out small differences which would be obscured in tests on the former. Moreover, since the Goodrich plastometer measures two factors, softness and retentivity, the exact nature of the changes produced by heating are easily visualized. It is generally, but not invariably, true that both the softness factor and the retentivity vary in the same way with different treatments of the same compound.

Three methods have been used in this study.

METHOD 1—The temperature coefficient of plasticity is measured. The differences in the curves for compounds which set up at relatively low temperatures and those which do not are shown in Figure 1. The sharp break in curve 3 at a temperature near 90° C., and the marked decrease in plasticity above this temperature are evidence that the stock has been cured fairly tight in the preheating time of 30 minutes, the time required to assure that the test pieces are uniformly warmed throughout. The other two curves, one for crude rubber and the other for a slow curing compound, follow the normal course expected for these stocks. This method, however, does not lend itself to locate accurately either temperature or time of the beginning of cure, but it does afford a means of rough comparison between different compounds.

METHOD 2—The test pieces are heated in the plastometer furnace for intervals up to 3 hours at selected temperatures, and plasticity measurements made in the usual fashion. The types of curves obtained by this method are given in Figure 2, curves 1 and 3. If the stock is non-scorching at the testing temperature, the plasticity rises and remains at constant value after the test piece is thoroughly heated, for the duration of the heating period, as illustrated by curve 3. If the stock tends to scorch, however, the plasticity values show a sharp decrease with or without a period of constant plasticity. The behavior of such a compound is illustrated by curve 1. Here again the location of the onset of cure is difficult to measure with accuracy, for this involves the determination of the deviation of the time-plasticity curve from the normal course of the curve representing the stock under non-scorching conditions.

METHOD 3—The test pieces are prepared and heated at selected temperatures for various intervals in an air oven, quickly cooled, and then tested at room temperature which has been standardized at 30° C. (86° F.). If no change has occurred, the plasticity values will lie along a horizontal line parallel to the time axis. Deviations from this line

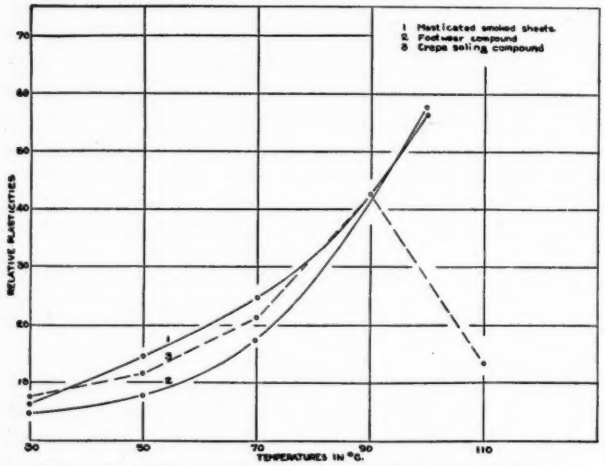

Figure 1—Temperature Coefficients of Plasticity for Three Rubber Compounds

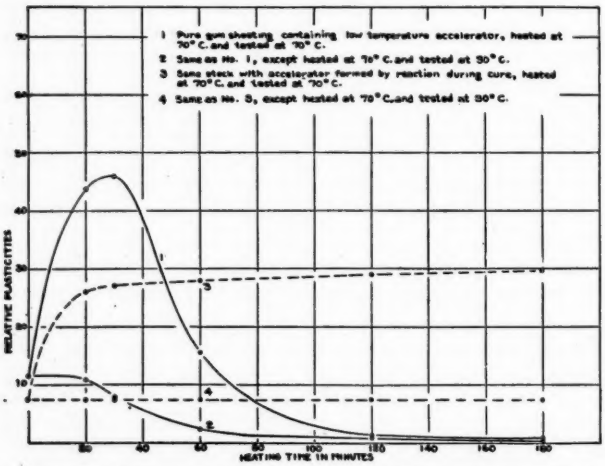
1 Pure gum sheeting containing low temperature accelerator, heated at 70° C. and tested at 70° C.
2 Same as No. 1, except heated at 70° C. and tested at 30° C.
3 Same stock with accelerator formed by reaction during cure, heated at 70° C. and tested at 70° C.
4 Same as No. 3, except heated at 70° C. and tested at 30° C.
RELATIVE PLASTICITIES
HEATING TIME IN MINUTES

Figure 2—Comparison of Two Methods of Measuring Scorching of Rubber Compounds

downward generally indicate that cure has taken place, and the length of time elapsing before such departure is a measure of the safe time of storage at the temperature of test. Figure 2, curves 2 and 4 represent a scorching and a non-scorching compound, respectively, heated at 70° C. (158° F.), and correspond to curves 1 and 3 in the same

figure. The definiteness of the beginning of cure in curve 2 as compared with curve 1 is well illustrated by this example.

Unless the compounds are air-curing, the results are not affected if the test pieces are not measured immediately upon thorough cooling. For certain stocks measurements made as long as 24 hours after cooling have shown the same values as those made less than an hour after cooling.

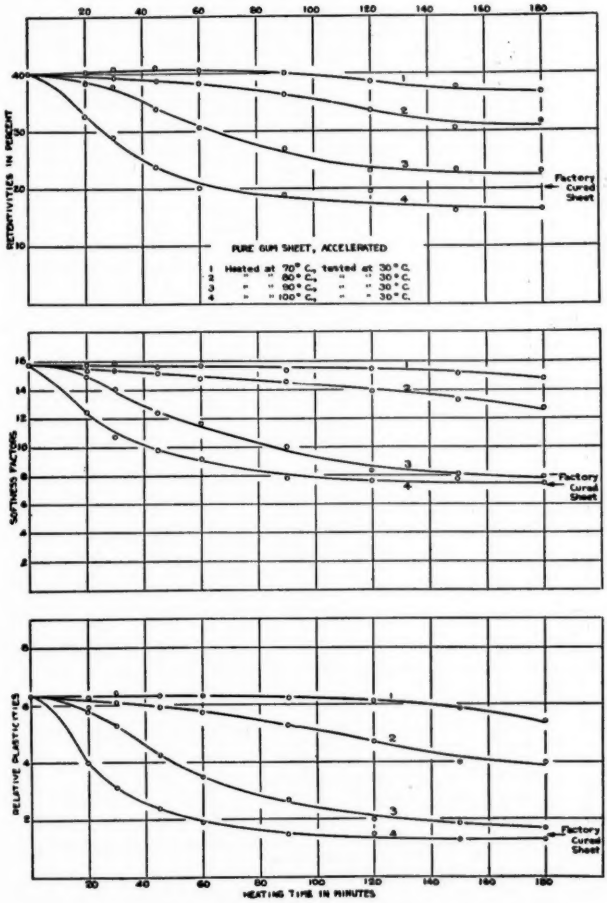
RETENTIVITIES IN PERCENT
SOFTNESS FACTORS
RELATIVE PLASTICITIES
HEATING TIME IN MINUTES
Factory Cured Sheet
PURE GUM SHEET, ACCELERATED
1 Heated at 70° C., tested at 30° C.
2 " " 80° C., " " 30° C.
3 " " 90° C., " " 30° C.
4 " " 100° C., " " 30° C.

Figure 3—Time-Temperature Changes in Retentivity, Softness Factor, and Plasticity of Accelerated Rubber Compound

For convenience it is preferred to preheat the test pieces in a mold in an air oven. The mold consists of a steel tray containing a series of bars in which are drilled holes just slightly larger than the diameter and slightly deeper than the height of the test pieces. In the apparatus used, each bar can accommodate twelve test pieces and is stamped at the end with the number corresponding to the interval of

preheating. In this way a number of compounds, up to six, may be simultaneously heated and conveniently removed at the proper time. During the preheating, the mold is closed by a heavy steel lid to prevent longitudinal distortion of the test pieces. Before loading, the mold is brought to the desired temperature, either in a platen press or in the air oven.

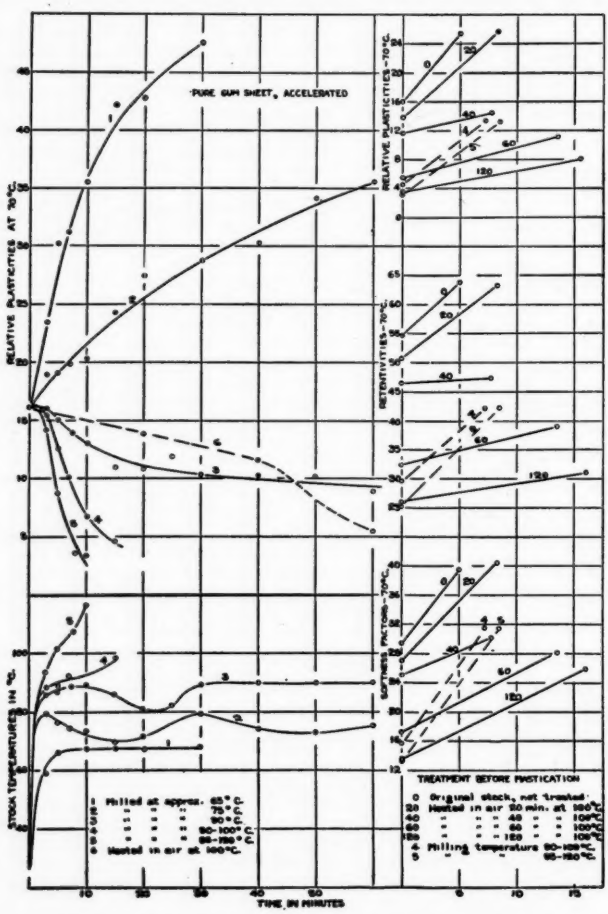
PURE GUM SHEET, ACCELERATED
RELATIVE PLASTICITIES AT 70°C.
RELATIVE PLASTICITIES-70°C.
RETENTIVITIES-70°C.
SOFTNESS FACTORS-70°C.
STOCK TEMPERATURES IN °C.
TIME IN MINUTES
TREATMENT BEFORE MASTICATION
0 Original stock, not treated
20 Heated in air 20 min. at 100°C.
40 " " " 40 " " 100°C.
60 " " " 60 " " 100°C.
120 " " " 120 " " 100°C.
4 Milling temperature 80-100°C.
5 " " 95-120°C.
1 Milled at approx. 65°C.
2 " " " 75°C.
3 " " " 90°C.
4 " " " 80-100°C.
5 " " " 95-120°C.
6 Heated in air at 100°C.

Figure 4—Milling Tests for Rubber Stocks Scorched by Prolonged Heating and by Milling

Comparison of Results

In general it has been found that, for a given compound, the progress of the changes in the softness factors, retentivities and plasticities, follows the same course for different treatments, such as mastication and aging, although this is not invariably true. An illustration of this behavior in cure is given in Figure 3 in which the parallelism of the three factors is evident. It may be noted that the factory cure for

this compound is the equivalent of 45 minutes at 144° C. (280° F.), yet at 100° C. (212° F.) a definite cure has occurred within 20 minutes. As judged by the downward deviation of the plasticity-time curves, storage at 70° C. (158° F.) for any long interval would be decidedly detrimental to the calendering properties of the compound, approximately 2 hours being the safe time limit.

Practical Application

The translation of the observed plastometric effects into factory operations is of great practical importance. For example, for the highly accelerated compound illustrated in Figure 3, the mixing time is 26 minutes for 50-pound (22.68-kg.) batches on 60-inch (1.52-meter) mills, the roll temperature of which is specified not to exceed 52° C. (125° F.). The temperature of the warm-up mills is maintained at the

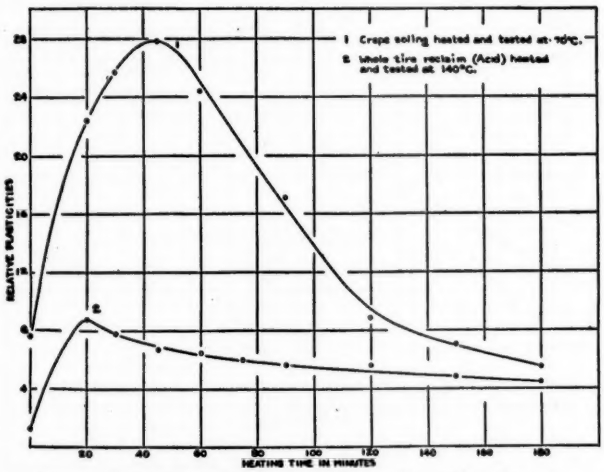
1 Crepe soling heated and tested at 70°C.
2 Whole tire reclaim (Acid) heated and tested at 140°C.
RELATIVE PLASTICITIES
HEATING TIME IN MINUTES

Figure 5—Comparison of Curing Effect and Heat Stiffening in Rubber Compounds at Elevated Temperatures

same figure. Calender temperatures are not allowed to exceed 88° C. (190° F.) and small feeds are specified. Under these conditions the stock may be processed successfully.

It is also of interest to note that the plasticity factors for this compound in the form of the factory-cured product are equal, within the limits of production variations, to those of the test pieces heated for about two hours at 100° C. (212° F.). It has been stated that the most important difference between vulcanized and unvulcanized rubber lies in the disappearance of the plastic state of the material; it has been found, however, that all the compounds so far studied possess measurable plasticity in the cured condition.

Milling and heating tests for samples from factory-mixed batches of this compound are illustrated in Figure 4. The lower left-hand curves represent the temperature changes in the stock when milled in 1-kg. (2.2-pound) batches on

small laboratory mills, 15 × 30 cm. (6 × 12 inches). The corresponding plasticity changes are shown by the group of curves in the upper left-hand portion, with the addition of a curve showing the changes produced by heating in air at 100° C. The end points for curves 4 and 5 corresponding to milling periods of 10 and 15 minutes at 90° to 120° C. represent badly scorched stocks. This is equally true of the batch heated 60 minutes at 100° C., curve 6.

The plasticity increases produced in these batches upon further mastication and cooling are shown in the curves in the right-hand portion of Figure 4. It is at once evident that the effects produced by heat and by milling at high temperatures are not of the same nature, as indicated by the rate of change of plasticity factors. In the case of the batches scorched by milling, the rates of increase are approximately the same as for the original stock, while for the batches heated

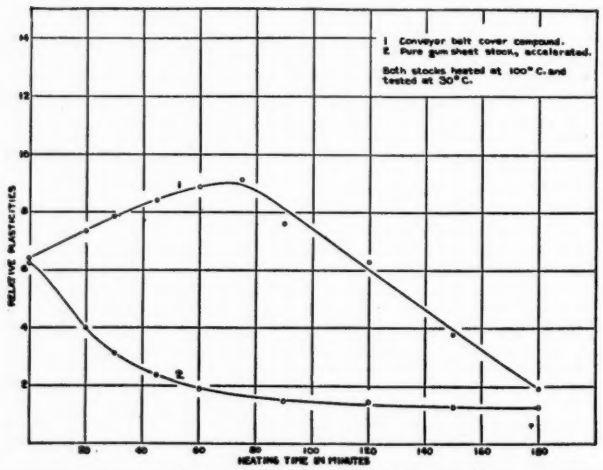
1 Conveyor belt cover compound.
2 Pure gum sheet stock, accelerated.
Both stocks heated at 100° C. and tested at 30° C.
RELATIVE PLASTICITIES
HEATING TIME IN MINUTES

Figure 6—Heat Softening Followed by Stiffening Compared with Usual Scorching at 100° C.

in air from 20 to 120 minutes, the rate of plasticizing is progressively reduced as the time of heating becomes longer. Moreover, the retentivity factor is affected more than the softness factor—that is, on milling the stock remains more "nervy" although it appears to soften to a satisfactory degree.

Other interesting effects of prolonged heating upon the plasticities of unvulcanized rubber compounds are illustrated in Figures 5 and 6. In Figure 5 the difference between scorching (curing) and heat stiffening is shown. Curve 2 demonstrates the gradual stiffening of a whole-tire acid reclaim. This cannot be considered cure, at least in the ordinary sense, on account of the previous devulcanization history and the low free sulfur content of the sample, approximately 0.1 per cent. Figure 6, curve 1, demonstrates another effect sometimes observed, in which the compound first gradually

increases in plasticity, then, as heating continues, gradually stiffens. This, also, cannot be considered scorching such as is illustrated by curve 2 obtained for another compound under exactly similar conditions. The plasticity changes illustrated by the curves in Figures 5 and 6 are not transient effects, since at least 24 hours elapsed between heating and testing. These latter effects are generally observed in low-grade stocks of relatively low plasticities, but are nevertheless of importance in factory operations, and their elimination by proper compounding effects improvement in processing.

Literature Cited

(1) Karrer, Davies, and Dieterich, IND. ENG. CHEM., Anal Ed., **2**, 96 (1930).
(2) Krall, IND. ENG. CHEM., **16**, 922 (1924).
(3) Thies, *Ibid.*, **20**, 1223 (1928).
(4) Winkelmann and Croakman, *Ibid.*, **22**, 965 (1930).

[Reprinted from Industrial and Engineering Chemistry, Vol. 23, No. 7, page 824. July, 1931.]

Value of Softeners in Tread Stock[1]

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The effect of three common softeners on the wearing qualities of a Captax-accelerated tire-tread stock is shown and comparison is made of road-wear ratings with the common laboratory tests.

The effect of any quantity of either pine tar or mineral rubber is to decrease the road-wear resistance. A content of approximately 4 per cent stearic acid is shown to give the best tread wear.

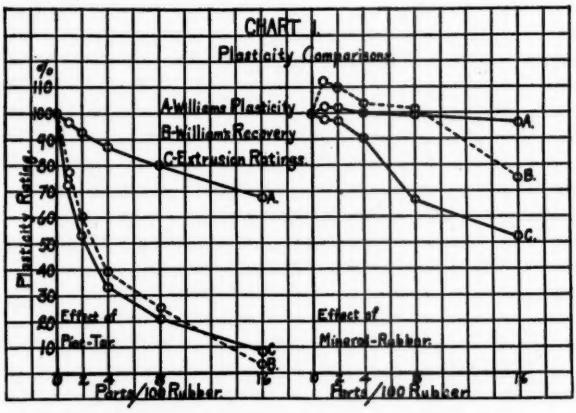
The common laboratory tests give results in the same direction as the average road wear with the 30 per cent slip abrasion test giving the best agreement.

SOFTENERS are used in tire-tread compounds essentially for facilitating factory processing. This is accomplished through their ability to produce more plastic stocks and thus permit smooth processing at lower temperatures. Certain softeners possess other valuable properties, such as favorable effects on dispersion, bloom, tack, activation, anti-scorching, etc., and quite often such materials are compounded primarily for one of these reasons rather than for their softening action.

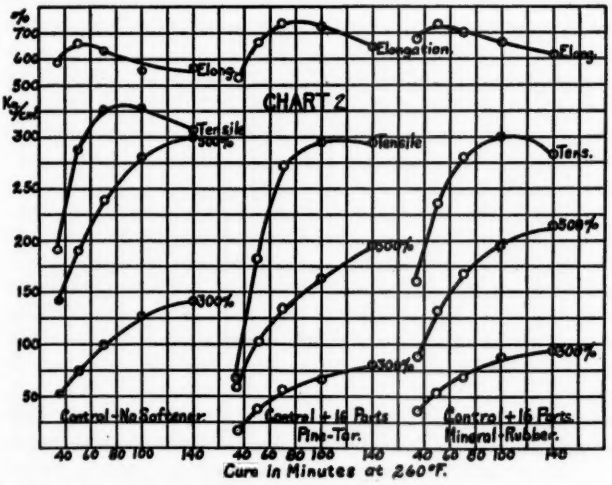
From a cost standpoint, the efficiency of certain softeners in producing a given plasticity in less time and with less mechanical work than is otherwise required is to be considered. Most common softeners have a lower volume cost than rubber, and their addition to a compound therefore lowers compound costs. In any event the addition of softeners, for whatever purpose, is made with full cognizance on the part of the compounder of their subsequent effects on the cured properties of the stock and on product performance.

[1] Received April 10, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Previous work on softeners has been confined largely to studies of their effects on the physical properties of both cured and uncured stocks, and has been directed toward means of evaluating new materials in terms of current ones and toward classifications by means of which this large group of ma-



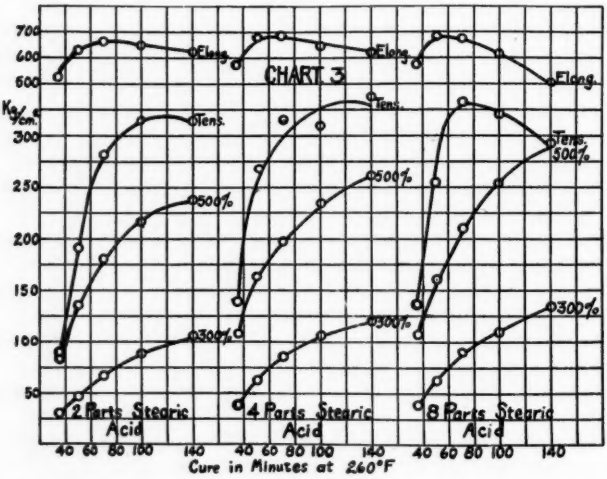
terials might be more intelligently used. Burbridge (*2*) presents a comprehensive survey of the effect of softeners on plasticity and tensile properties and, in a later work (*3*), of their effect on aging. He proposes two classifications, true softeners and pseudo-softeners, the former being those which enter into the rubber nucleus and produce a swelling action, and the



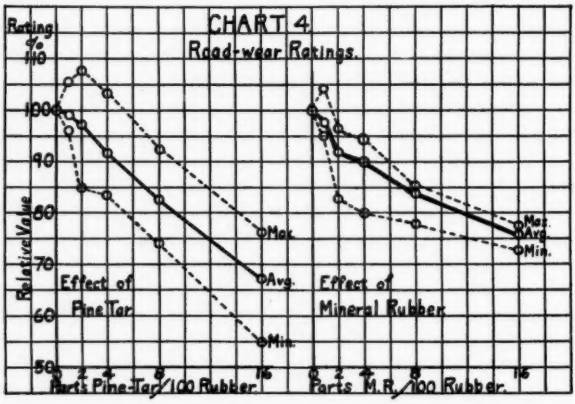
latter, those which do not and impart merely a lubricating action by surrounding the particles. Aultman and North (*1*) made a study of the depolymerizing and swelling action of softeners on samples of cured rubber. Zimmerman and Cooper (*9*) arrived at a numerical evaluation of a series of

softeners and proposed another classification—namely, anti-softeners as opposed to softeners. Their work is confined to uncured stocks.

It is the purpose of this work to consider three softeners from the standpoint of product performance based on tread-



wear measurements and to compare these results with those obtained in the current laboratory tests. Since the quantity of softener used in a given stock is determined largely by the individual factory machines on which the stock is to be run, no attempt has been made to recommend any softener ratios.



However, the stocks studied include all normally compounded ratios and their relative plasticity has been determined on two instruments believed to give reliable indications of tread processing, so that from these data some idea may be gained of the handling properties of these stocks.

Materials

The three softeners studied were pine tar, mineral rubber, and stearic acid. All three were taken from large commercial lots and had the following properties:

Pine tar: Specific gravity at 60° F., 1.065; viscosity (Stormer) 50 gram weight at 75° F., 12; initial boiling point, 90° C.; 10 per cent distilled, 206° C.; 30 per cent distilled, 280° C.; 80 per cent distilled, 358° C.

Mineral rubber: Melting point (cube method), 170° C.; penetration at 75° C., 94.

Stearic acid: Melting point, 52.5° C.; acid number, 208; saponification number 209; iodine number, 11.1.

Compounding

In compounding the pine tar and mineral rubber one base stock containing 4 parts of stearic acid per 100 rubber was used. The composition was as follows:

	Parts
Rubber	100.00
Gas black	40.00
Zinc oxide	5.00
Sulfur	3.00
Captax	1.25
Stearic acid	4.00
Softener	Varied 0, 1, 2, 4, 8, and 16

The effect of pine tar and mineral rubber on cure was regarded as slight in this stock, and no adjustment of vulcanization ingredients was made for this reason.

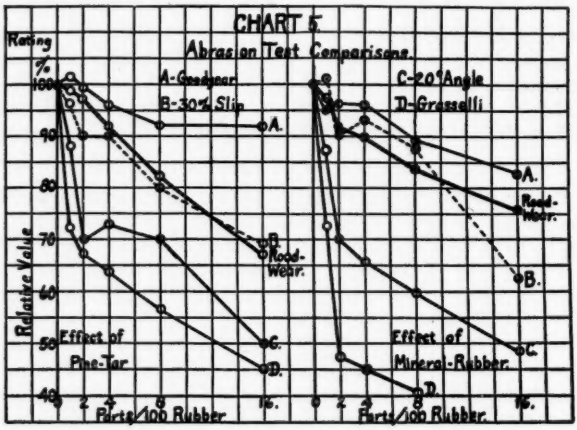
Stearic acid, while possessing considerable softening action, has a distinct activating effect on Captax in this stock and is used primarily for this reason. A comparison was made of the effect of varying stearic acid in the stock containing 4 parts of pine tar per 100 rubber. The three ratios of stearic acid selected were 2, 4, and 8 parts per 100 of rubber. The effect of reduction of stearic acid in lowering tensile properties was realized, but the writers' interest lay in testing a stock of this composition regardless of tensile properties.

Plasticity Tests

Chart 1 shows the plasticity ratings for varying amounts of pine tar and mineral rubber. The plasticities of the stocks containing softener are expressed as per cent of the control, containing no softener. A lower rating indicates a softer stock. The Williams plastometer (*8*) readings were taken at 70° C. and express the thickness of a 2-cc. pellet after 3 minutes under a 10-kg. load (curve *A*). The recovery (curve *B*) is the recovery in thickness 1 minute after removal from the press. The extrusion plastometer ratings (curve *C*), determined on a modified Marzetti (*5*) type of instrument, are based on the volume of stock extruded through a standard orifice at 63° C. under a pressure of 14.06 kg. per sq. cm. (200 pounds per square inch). In this case the reciprocals of the actual values have been plotted so as to have a decreasing rating with softer stocks.

The softening action of increasing amounts of pine tar is

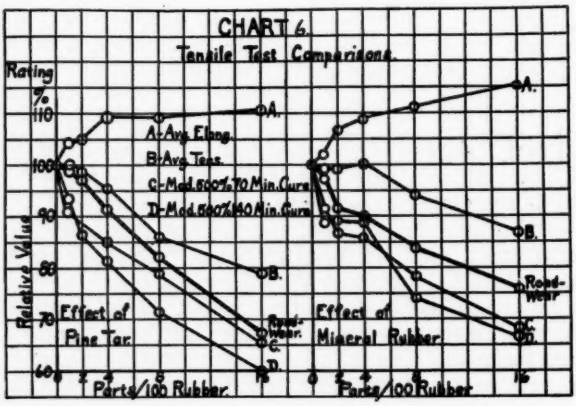
evident from the Williams plastometer data, but the effect of mineral rubber, which is known to facilitate tubing, is not shown in this test. In fact, the recovery values indicate a stiffening action while the plasticity values remain approximately equal to that of the stock containing no softener. The



extrusion plastometer satisfactorily demonstrates this softening action and indicates that pine tar is more effective as a softener than mineral rubber.

Tensile Tests

The tensile properties of these stocks may be seen on Chart 2, where the control and the stocks containing the extreme



loadings of softener are shown. The data of all intermediate stocks lie between the control and the extremes. The effect of these two softeners in lowering the modulus and tensile of cured stock is evident, pine tar softening to a slightly greater degree than mineral rubber. This softening action

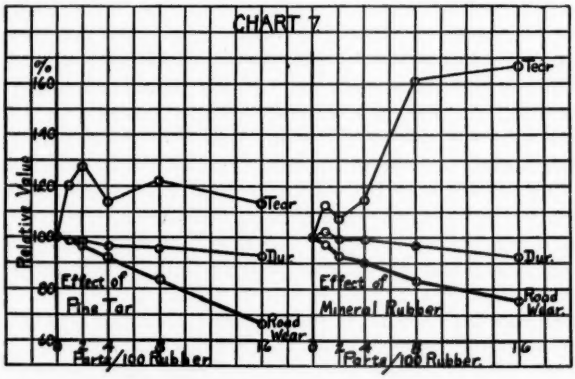
was perceptible with the addition of one part of either of these materials.

There is a retardation of cure to be observed on Chart 2 in the tensile graph for the stock containing 16 parts of pine tar. This is not great and is scarcely perceptible with 8 parts of pine tar. It was therefore deemed unnecessary to alter an orderly comparison by an adjustment of cure.

Chart 3 shows the data for the stearic acid stocks. Here the effect on modulus and tensile is in the reverse order, in that with increasing stearic acid the modulus and tensile are improved. This is due to the activating effect of stearic acid, which in excessive amounts produces a stock of relatively short range.

Road Tests

The road tests on these stocks were made on some two hundred 30 × 5 six-ply truck type tires run in taxicab service in Philadelphia. The test began in August, 1929, and was completed in the late spring of 1930. Stocks were compared



by making one half of the tire of control stock and the other half of the stock containing the softener. In comparing stocks 1, 2, and 4 per cent pine tar or mineral rubber were run against 0 per cent as a control, while the 8 and 16 per cent stocks were run against 4 per cent as a control and the latter ratings calculated in terms of 0 per cent softener. This was done to preserve tire balance as much as possible and to prevent errors due to large differences between two stocks on the same tire. The tires were measured prior to running on the road and when worn to approximately one-third of their original button height. Two methods of measurement were used—namely, the button height method which determined button height above the base of the grooves, and the over-all method which measured the total change in thickness of the tire by means of a caliper device. The data from these two methods checked within reasonable limits, and the average was used for computing losses and ratings.

Chart 4 shows the rating values for the addition of pine tar

and mineral rubber. Each point on these curves represents the average of at least ten tires. The maximum and minimum ratings are also shown, so that some concept of variation in behavior of stocks under different road conditions may be obtained. The distribution of the ratings between the maximum and minimum values, in general, shows a peak around the average rating, although there are intermediate ratings so that the maximum and minimum values are by no means isolated points.

The net effect of either of these materials is to decrease the road-wear resistance, mineral rubber causing more marked decreases than pine tar when added in small amounts. However, beyond 4 per cent it shows distinctly better resistance and throughout the range shows less variation from the average values. The fact that maximum values show ratings above the control for the addition of small amounts explains the occurrence, at times, of tests which indicate an improvement with the addition of such materials.

It is realized that the method of compounding here used, in which the softeners were added to a base mix, changed the percentage volume loading of gas black in the compound. The other method would have been to hold the percentage volume of gas black constant. If the base-mix method is considered on the percentage-by-volume basis, it will be found that the gas-black content has been reduced by approximately 2 per cent in the stocks containing the maximum loading of softener. Based on a number of road tests, such a reduction in loading would decrease tread wear by not more than 8 per cent and this decrease would, of course, diminish as the percentage of softener is decreased. Therefore the average tread-wear curves shown on Chart 4 might be displaced upward slightly at their lower extremities, but such changes would be insufficient to alter the conclusions.

The effect of stearic acid on tread wear may be seen in Table I.

Table I—Effect of Stearic Acid on Tread Wear
(Base stock plus 4 parts pine tar plus stearic acid)

Stearic Acid in Stock	Rating		
	Av.	Max.	Min.
Parts	%	%	%
2	95	97	90
4	100	100	100
8	97	106	92

These data apply to the three stocks whose tensile properties are shown on Chart 3. From them we can conclude that the optimum ratio of stearic acid for this stock is approximately 4 parts per 100 of rubber.

Abrasion Test Comparison

The abrasion test comparisons are shown in Chart 5. The various methods used have been fully described by Vogt (7) and therefore will be described only briefly here. The designation of the method coincides with that used on Chart 5.

Method A—Regular Goodyear machine, 16-degree angle
Method B—30 per cent slip machine
Method C—20-degree angle machine
Method D—du Pont–Grasselli abrader

Examination of this chart shows method B to produce data most comparable with the road-wear ratings. Method A in each case lies above the road wear, while methods C and D are considerably below. It might be remarked in this connection that Lambourn (*4*) has found a variable slip machine to give very good agreement with road-wear values and the present data lend support to such a conclusion.

The data in Table II were obtained from the stearic acid stocks using methods A and D.

Table II—Effect of Stearic Acid on Abrasion Resistance
(Base stock plus 4 parts pine tar plus stearic acid)

Stearic Acid in Stock	Av. Road Wear	Method A	Method B
Parts	%	%	%
2	95	87	98
4	100	100	100
8	97	109	109

The high ratings of the stock containing 8 per cent stearic acid are, no doubt, due to the lubricating action of an excess of this material, which has been previously reported by North (*6*).

Tensile Test Comparisons

These comparisons are shown on Chart 6. Curve *A* represents the average elongation of a series of five cures; curve *B*, the average tensile; curve *C*, the modulus of the 70-minute or best cure at 500 per cent elongation; and curve *D*, the modulus of the 140-minute cure at 500 per cent elongation.

The elongation increases, as would be expected, with increased softener, while the modulus and tensile values are decreased, as indicated on Chart 2. The average tensile does not decrease so rapidly as the average road wear, but the modulus values drop off more rapidly. These values are not so widely divergent as the abrasion data, but no single one of them presents an accurate index of road-wear resistance.

Tear Test Comparisons

On Chart 7 are shown the ratings of a tear test described in an unpublished work of G. J. Albertoni, of this laboratory. This test employs a rectangular test piece cut from standard laboratory test sheets. The dimensions are approximately 7.62 by 5.08 cm. (3 by 2 inches) with the length in the direction of the grain. A cut is made with the shears 2.54 cm. (1 inch) long in the center of the test piece in the direction of the grain. Two jaws are then fastened to the sample approximately 1 mm. from the edge of the cut. One jaw is 2.54 cm. (1 inch) wide and extends over the length of the cut, while the other is 7.62 cm. (3 inches) wide and ex-

tends over the entire width of the test piece. The jaws are separated on a Cooey machine and the pull is recorded. The test is an effort to duplicate the conditions of hand tear.

It will be seen on Chart 7 that the tear is measurably improved with the addition of softeners and that mineral rubber produced more improvement than pine tar. The durometer ratings of the tires after curing are also shown on this chart. The hardness of the stock containing no softener was 62 and that of the stock containing the maximum of softeners, 57.

Economy

From an economic standpoint the savings to be effected by the use of softeners are dependent on a number of processing advantages which are impossible to evaluate in accurate cost figures. For this reason simple compound costs do not tell a complete story.

However, if softeners are to be effective as a means of giving lower quality tread stocks at a lower volume cost, the decrease in cost should be the same as the decrease in quality as the softener is increased. With the present prices on rubber and other compounding ingredients, this order does not hold. For example, with the addition of 16 parts of pine tar the compound cost is reduced to 93 per cent of that of the control, while the tread wear is reduced to 67 per cent. In the case of mineral rubber the cost is reduced to 92 per cent while the tread wear is reduced to 75 per cent.

Conclusions

In view of these results, it may be concluded that in this tread stock the minimum amount of pine tar or mineral rubber commensurate with good factory processing is desirable if the maximum abrasion resistance for a given cost is to be obtained. This means that softeners which are effective, as such, in smaller amounts than those available at present should find a use in tread compounding. Stearic acid should be held to a ratio of approximately 4 parts per 100 of rubber.

Most of the laboratory tests give indications in the same direction as the road wear, but none coincide exactly.

Acknowledgment

The authors desire to acknowledge the work of C. R. Park, formerly of this laboratory, in the initial planning of these experiments, and to express their thanks to R. P. Dinsmore for permission to publish this paper.

Literature Cited

(1) Aultman and North, IND. ENG. CHEM., **15**, 262–4 (1923).
(2) Burbridge, *Trans. India Rubber Inst.*, **1**, 429 (1926).
(3) Burbridge, *Ibid.*, **2**, 256–66 (1926).
(4) Lambourn, *Rubber Chem. Tech.*, **2**, 166–92 (1929).
(5) Marzetti, *Giorn. chim. ind. applicata*, **5**, 342 (1923).
(6) North, IND. ENG. CHEM., **21**, 722–3 (1929).
(7) Vogt, *Ibid.*, **20**, 140–9 (1928).
(8) Williams, *Ibid.*, **16**, 362 (1924).
(9) Zimmerman and Cooper, *Ibid.*, **20**, 812–3 (1928).

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Influence of Physical Properties of Carbon Black on Its Tinting Strength[1]

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The results obtained by investigating the effect of compression, moisture, absorbed gases, heating, surface tension depressants, and deflocculation on the tinting strength of carbon black are presented. From these experimental data it is concluded that tinting strength is not an absolute function of particle size, and is inversely proportional to gases adsorbed on the individual particle surface. This indicates the physical properties of carbon black to be mainly in agreement with some recent theories presented.

IN VIEW of the extensive investigations dealing with the influence of the physical properties of commercial pigments on their suitability as coloring agents for paint and inks, it is surprising that the data available in the literature relative to the evaluation and utilization of carbon (gas) blacks, or color blacks as they are known to the trade, should be so meager.

It is now generally known in the trade that the importance of this pigment is to a large extent directly attributable to its fine state of division, recent investigators having determined the average individual particle to be of colloidal dimension and thus beyond the resolving power of an ordinary microscope. Unfortunately, however, such a fine state of division is necessarily accompanied by high oil absorption and, as pointed out by Barnard (*2*) and Wagner

[1] Received April 9, 1931. Presented before the Division of Paint and Varnish Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

and Pfanner (*17*), the oil absorption of a pigment is a function of the exposed surfaces and the increase in oil absorption proportional to the fineness of division. Grohn (*10*) further suggests that the vehicle absorption of a pigment is influenced by the nature of the vehicle, the type and particle size of the pigment, and their mutual absorptive capacities.

Distinct from the majority of other important pigments, carbon blacks possess the property of adsorbing gases or vapors, both during the process of manufacture and subsequently during exposure to the atmosphere. This phenomenon has been investigated by Johnson (*13*), who states that the quantity of gases adsorbed on the surface of the carbon-black particle will vary with the physical characteristics. Such adsorbed gases create a protective film around the individual particle and, as pointed out by Klumpp (*14*), since these films are of relatively considerable diameter, there is a great tendency to increase the oil absorption.

The properties of the dispersing medium are extremely important in determining the oil absorption of carbon black, as this medium is directly responsible for the degree of wetting which takes place. Bartell and Smith (*5*), Bartell and Hershberger (*4*), and Osterhof and Bartell (*16*) attribute such variations in wetting to the facility with which the adsorbed gases are disentangled, and McMillan (*15*) suggests this efficiency in wetting properties to be a function of the angle of contact and the adhesion tension of the dispersing medium.

In a certain measure it seems probable that oil absorption and tinting strength of carbon black should be controlled by the same influences, the latter, as shown by Briggs (*6*), depending theoretically at least on (*a*) the relative size of the particle, (*b*) the extent to which the smaller particles adhere to the larger ones, and (*c*) the hiding power at constant size of the smaller particles. Briggs further states that the tinting strength of a particle cannot be used as a measure of opacity unless the size relations and adhesion factors are kept constant. If such is the case, one must concur with Gardner (*8*) that there is no definite relation between the tinting strength of a pigment and its hiding power, and hence that there must be influences other than those stated by Briggs equally responsible for the degree of tinting strength possessed by various blacks.

If these previously mentioned films of adsorbed gases are considered from the standpoint of the selective adsorption theory, as stated by Fink (*7*) and Heaton (*11*), the following points present themselves: (1) These gaseous films existing around the particle will prevent perfect adherence of the smaller particles to the coarser ones; (2) the gaseous film at the interface, being of varying thickness, creates voids through which the light will be reflected; and (3) the varying refractive indices of the gases, owing to their constituency, will determine the nature of the reflected light.

It has been for the purpose of determining the nature and degree of the role played by such gaseous films, present in varying proportions on the surface of color-black particles, on its tinting strength, that the present investigation was undertaken.

Experimental Methods

Standard methods of evaluation were employed exclusively as follows:

Oil-absorption numbers were determined by the method described by Heaton (*12*).

Rub-outs with a glass muller, using Green Seal zinc oxide and refined linseed oil as diluents, were used in obtaining

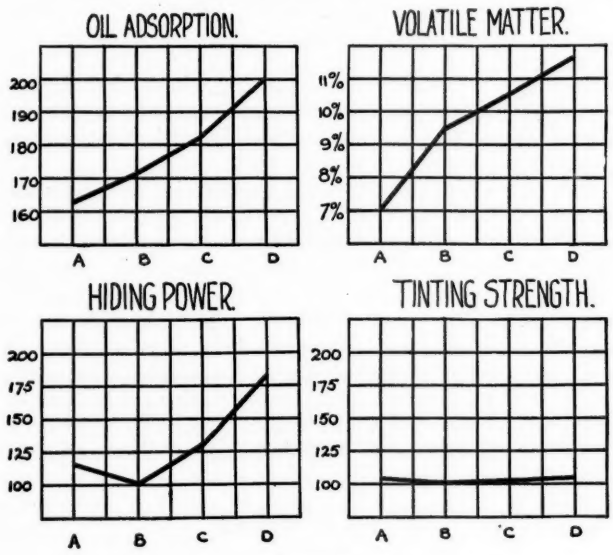

Figure 1

the tinting strength, which was determined quantitatively in all instances.

The amount of volatile matter was obtained by the method reported by Johnson (*13*).

Moisture determinations were carried out for 2 hours in a constant-temperature oven at 110° C., the sample being spread in aluminum pans with close-fitting tops.

Interfacial tension of the dispersing mediums was measured by the method described by Gardner (*9*), a Donnan pipet being employed and all readings taken at 20° C.

Samples for compression experiments were prepared in a laboratory compressor especially designed for the work.

Effect of Particle Size

Four samples of carbon black manufactured under conditions productive of progressive decrease in particle size

were examined for hiding power, tinting strength, volatile matter, and oil absorption, the values obtained being presented graphically in Figure 1.

As expected, the values obtained for volatile matter and oil absorption evidence a progressive increase inversely proportional in the particle size. However, in the curves representing the hiding power and tinting strength a decided dip is evidenced, especially emphasized in the case of hiding power. The explanation that suggests itself assumes these curves to be a measure of two factors of opposed influence, one directly increasing in value as the particle size decreases, while the second, owing to greater thickness of the gaseous film surrounding the particle consequent on increased volatile matter, tends to decrease the values obtained.

Effect of Compression

A sample of black was subjected to increasing degrees of pressure and examined at the various stages of compactness. The tinting strength varied inversely with the pressure (Figure 2*A*).

It is to be expected that during compression agglomeration of the particles takes place, the size and number being commensurate with the degree of pressure applied. It was believed, therefore, that the effect on the tinting strength was probably due to insufficient deflocculation during the rub-out caused by the limited wetting possible with linseed oil. To establish this point definitely, further rub-outs were made with the addition of a surface-tension depressant, which would insure complete deflocculation. The results, as shown in Figure 2*B*, indicate that when deflocculation is complete precompression of a black has no direct influence on its tinting strength.

Effect of Heating

To ascertain to what extent removing the adsorbed gases from the carbon-black particle would affect its tinting strength, various samples representing different grades of blacks were subjected to a series of heat treatments ranging from 110° to 950° C. As will be seen from Figure 3, the tinting strength increases proportionately to the temperature or, in other words, inversely to the extent of the adsorbed gases present.

Discussion

The results agree well with the findings of Wagner and Pfanner (*17*) in that the oil absorption of carbon (gas) black is directly influenced by the particle size. Considerable evidence has also been secured to show the results reported by Klumpp (*14*), Grohn (*10*), and Baldwin (*1*) on other pigments—that the presence and amount of adsorbed gases and the nature of the vehicle exert considerable influence

on the oil-absorption values—also maintain for carbon black.

The present experiments indicate that these factors have a very direct bearing on the tinting strength of a carbon black. It has not been possible to demonstrate any direct ratio between particle size and tinting strength, and it will be noted that, although in the series in which the hiding power, and hence necessarily the particle size, exhibit definite variation, the tinting strength may remain practically constant.

If the tinting strength is a direct function of selective adsorption of the fine particles to the coarser ones (*6*), then by decreasing the particle size of the black we would not only increase its hiding power but proportionally increase its tinting strength. Of course, the opacity of the reducing agent must be taken into consideration to some extent and, although the grouping effect of the black particles around the zinc oxide particles is partially responsible, other important factors are involved. However, the volatile-matter and oil-absorption values indicate variations not attributable to particle size, and in all probability an actual variation in the thickness of the surface films of adsorbed gases occurs. It therefore seems probable that a relationship maintains between the oil absorption and volatile matter and the tinting strength. The explanation that suggests itself is that such films of adsorbed gases, inasmuch as they vary in thickness, control the dimensions of the voids existing between the carbon-black particles, and thus, operating in conjunction with the variation of the refractive indices of the gases constituting such films, determine the amount of reflected light produced.

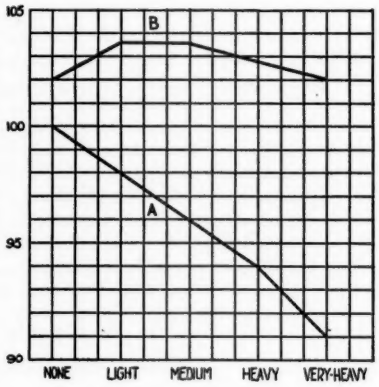

Figure 2—Effect of Compression

The ease with which these gases may be disentangled depends exclusively on the efficiency of the medium used, and complete deflocculation will therefore only be obtained when the dispersing medium is efficient enough completely to disentangle the adsorbed gases, and this efficiency will vary with thickness of the protective film of adsorbed gases present. Perfect wetting is only possible where the interfacial tension of the medium is sufficiently low to displace these adsorbed gases completely.

It was found that precompression had no direct influence

on the tinting strength of carbon (gas) blacks. Samples of black were compressed, the degree of compression ranging from "light to very heavy." Such compression caused agglomeration of carbon-black particles, the agglomerates increasing in size and number proportionally to the applied pressure. When rubbed out with a reducing agent and a diluent, the tinctorial power of the blacks decreased in direct proportion to the pressure. The theory submitted is that the film of gas that was adsorbed on the surface of the individual particle was displaced at the points of contact and took up a position around the agglomerate, thus increasing the thickness of the film. Owing also to this increased thickness of protective film, the affinity between the liquid and the pigment was decreased. As suggested by Bartell and Greager (*3*), the low adhesion of the medium may not

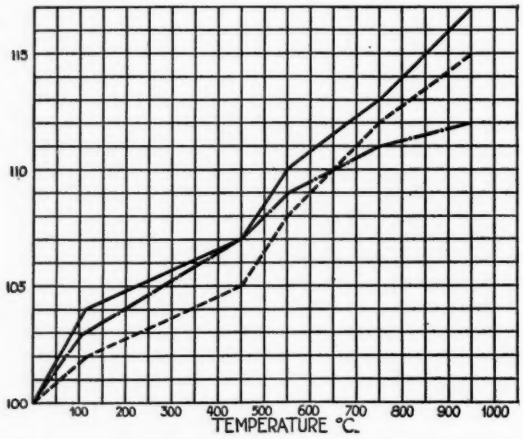

Figure 3—Effect of Heating

readily allow complete disentanglement of these gases, resulting in incomplete deflocculation of the agglomerates. It was found, however, that on the addition of an agent that would lower the interfacial tension and consequently raise the adhesion tension of the medium, this film surrounding the agglomerate could be readily disentangled, insuring practically a complete wetting of the particles. By such deflocculation the tinting strength was brought to the maximum.

The role played by the adsorbed gases was further demonstrated by heating carbon blacks at various temperatures. Eight samples of black, on being subjected to five different temperatures ranging from 110° to 950° C., showed that the tinting strength was inversely proportional to the volatile matter or adsorbed gases present.

The fact that water vapor is one of the constituents of the gases adsorbed by carbon black and is found in some instances, under ordinary conditions, in amounts as high as 8 per cent,

probably explains the improved tinting strength obtained by heating even at low temperatures (110° C.).

Flocculation of a black apparently commences at 450° C. and increases proportionally with the temperature. Such flocculation, however, was readily eliminated by lowering the interfacial tension of the medium.

Conclusions

1—Tinting strength is not an absolute function of particle.

2—No direct ratio exists between tinting strength and hiding power.

3—The thickness of the film of adsorbed gases on the carbon-black particles determines the tinting characteristics.

4—The volatile matter present and the oil-absorption properties serve as a measure of the relative thickness of such films.

5—The completeness with which these gases are displaced materially affects the tinting strength.

6—Complete displacement is only possible when the interfacial tension produced by the dispersing medium at the surface of the carbon-black particle is sufficiently low to assure complete wetting.

Literature Cited

(1) Baldwin, IND. ENG. CHEM., **21**, 326 (1929).
(2) Barnard, *Paint, Oil Chem. Rev.*, **70**, No. 1, 8 (1920).
(3) Bartell and Greager, IND. ENG. CHEM., **21**, 1248 (1929).
(4) Bartell and Hershberger, *Ibid.*, **22**, 1304 (1930).
(5) Bartell and Smith, *Ibid.*, **21**, 1102 (1929).
(6) Briggs, *J. Phys. Chem.*, **22**, 216 (1918).
(7) Fink, *Ibid.*, **21**, 32 (1917).
(8) Gardner, "Examination of Paints, Varnishes, Lacquers, and Colors," p. 59.
(9) Gardner, *Ibid.*, p. 288.
(10) Grohn, *Farben-Ztg.*, **33**, 1660 (1928).
(11) Heaton, "Outlines of Paint Technology," p. 12.
(12) Heaton, *Ibid.*, p. 24.
(13) Johnson, IND. ENG. CHEM., **20**, 904 (1928).
(14) Klumpp, *Farben-Ztg.*, **33**, 1044 (1928).
(15) McMillan, IND. ENG. CHEM., **21**, 1237 (1929).
(16) Osterhof and Bartell, *J. Phys. Chem.*, **34**, 1399 (1930).
(17) Wagner and Pfanner, *Farben-Ztg.*, **34**, 2513 (1929).

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Permeability of Rubber to Air

II—Effect of Stretch, Thickness, Milling, Compounding Ingredients, Kind of Crude Rubber, and Temperature of Vulcanization[1]

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In continuing the previous study of the effects of various factors on the permeability of rubber to air, it has been found that permeability varies inversely with thickness and with the volume of compounding ingredients present.

Factors having little or no influence on permeability include milling, kind of crude rubber used, and temperature of vulcanization.

The permeability of rubber was found to increase with stretch, the major factor involved probably being the accompanying reduction in thickness.

The applicability of certain of these results to the improvement of the air-retaining capacity of automobile inner tubes is obvious.

IN HIS comprehensive survey of the literature on the permeability of rubber to gases, Daynes (*3*) recently listed a number of factors concerning the influence of which on premeability there appeared to be no published information. The effects of milling, stretching, and the kind of crude rubber used were included among these factors. Daynes also indicated that the literature on the subject of compounding ingredients and the effect of vulcanization was rather meager.

[1] Received April 6, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

In this paper are presented certain data which have been obtained during an investigation of the effects of these and other factors upon the permeability of rubber to air. Although previous work has been done in connection with some of the phases studied, it has been carried out largely at pressures near atmospheric, with hydrogen as the gas involved, and with balloon fabrics as the membranes studied. Since the investigation herein reported was motivated by interest, not in the hydrogen-retaining capacity of balloons, but in the air-retaining capacity of thin sheets of rubber, the conditions under which the experiments were conducted were somewhat different from those of most previous investigators.

Apparatus and Method

The apparatus used in an investigation of the effects of temperature, pressure, and humidity on the permeability of rubber to air was described in a previous article (*11*). This equipment, hereinafter called apparatus A, was also used in part in obtaining the results reported below.

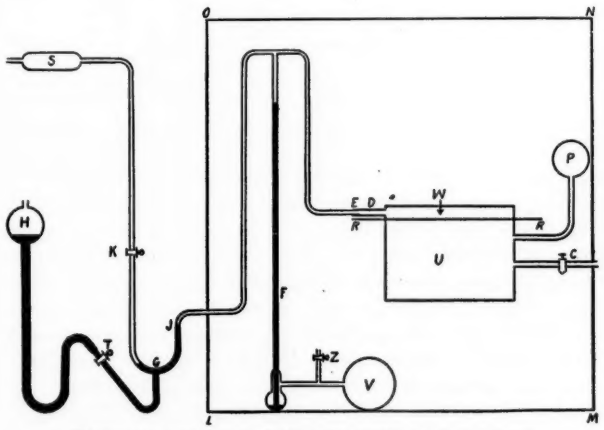

Figure 1—Apparatus B for Measuring Permeability

A modification, designated as apparatus B (Figure 1),[2] was used in certain of the present experiments. This equipment differed from apparatus A only in that the lower surface of the manometer fluid was not open to the air, but was connected to a chamber, *V*, which had a capacity of approximately 1000 cc. By means of this system it was possible to adjust the pressure on the manometer fluid at the beginning of an experiment, and maintain it practically constant throughout, regardless of the fluctuations of the barometric pressure of the atmosphere. The modified apparatus offered no great advantage in permeability measurements of short duration, but was less subject to error in the case of measure-

[2] The alterations in the original apparatus were made by J. W. Liska.

ments lasting several hours, such as the determination of the permeability of slabs cut from automobile inner tubes.

In brief, the method of measurement, which was previously described in detail for apparatus A (*11*), was to compress the air in *U* on one side of the rubber membrane *RR*, permit it to pass through the membrane into the slightly evacuated chamber, *W*, and observe the rate of fall of the manometer fluid in *F*. After a standard procedure had been adopted, the manometer was calibrated by introducing measured volumes of air and recording the consequent drop in the manometric column in centimeters per minute. It was found that the factor 3.35 will convert centimeters per minute to liters of air per hour per square meter of rubber exposed. The calibration was so conducted that the volume of air passing through in any subsequent experiment would be expressed under a pressure equal to that of the atmosphere when the stopcock, *Z*, was closed at the start of the experiment. The value for the volume thus obtained was then corrected to a barometric pressure of 760 mm.

The stock used in a majority of the experiments had the following composition:

	Parts
Smoked sheets	100.0
Zinc oxide	2.9
Sulfur	2.9
Di-*o*-tolylguanidine	0.6

Effect of Thickness of Rubber Film on Permeability

Daynes (*2*), working with hydrogen as the permeating gas, concluded that the permeability of a uniform film of rubber is inversely proportional to the thickness. In the same year Edwards and Pickering (*5*), also using hydrogen at atmospheric pressure, published results leading to the same conclusion. Since the latter investigators used samples from different sources and of varying composition, and not samples identical except for thickness, it seems to have been rather fortuitous that their results verified so well the simple relationship stated above. In a subsequent paper Daynes (*3*) mentioned that two other English investigators, Ritchie and Shakespear, had independently reached the same conclusion—i. e., that permeability is inversely proportional to thickness. Schumacher and Ferguson (*12*), however, in an investigation of the diffusion of water through rubber, obtained results indicating diffusion to be inversely proportional to a power of the thickness very near the second power. With very thin sheets the relation was somewhat different, but in no case was permeability inversely proportional to the first power of the thickness.

In the experiments described herein use was made of air at a pressure approximating that which exists inside an automobile inner tube in service. The pressure actually used was 46 pounds per square inch (3.23 kg. per sq. cm.). The rubber slabs were all cured for 30 minutes at 300° F. (149° C.).

The tests were conducted with apparatus A, the temperature being maintained at 30 ± 0.2° C. by means of the thermostatic control. The slabs were stretched 39.3 per cent in one direction immediately before they were clamped between the chambers *U* and *W*. All measurements except that on the 0.57-mm. slab were completed within 22 minutes after the slab had been placed in the permeameter. The thickness of a slab was obtained by averaging the values resulting from thirty to forty measurements with a Stickney gage made on various parts of that portion of the slab which was exposed to test. The thicknesses recorded are those of the unstretched slabs, whereas the permeabilities are those of the stretched slabs.

Table I and Figure 2 present the results of the permeability determinations and the calculated values for the impedance (reciprocal of permeability).

Table I—Effect of Thickness of Rubber on Permeability

Thickness		Permeability	Impedance
Mm.	*Inch*	*Liters/hour/sq. m. surface*	
1.01	0.040	0.11	9.1
0.97	0.038	0.12	8.3
0.79	0.031	0.15	6.7
0.67	0.026	0.18	5.6
0.57	0.022	0.25	4.0
0.47	0.018	0.30	3.3
0.31	0.012	0.58	1.7

It will be noticed that the value for the 0.57-mm. slab does not fall on the curve. This may be explained by the facts that its thickness was the least uniform of all the slabs and it was left stretched longer in the apparatus. It is apparent that the impedance is a linear function of thickness throughout the range investigated. Since the curve, if extended, would not pass through the origin, it is not justifiable to state with exactness that permeability is inversely proportional to thickness. This failure to pass through the origin is probably tied up with the fact that the measurements of thickness were not made on the stretched slabs. That permeability is approximately inversely proportional to thickness is certainly a justifiable statement.

In connection with the results obtained, it may be of interest to point out that many of the "super" tubes recently marketed by various rubber manufacturers have been unusually thick. Although an increase in the air-retaining capacity has probably not been the primary object of this "heavy gage," the fact remains that the extra thickness undoubtedly improves the inner tubes from the standpoint of permeability.

Effect of Stretching on Permeability of Rubber

Lambourn (*10*) has mentioned the desirability of making permeability measurements on stretched samples of rubber, if the results are to be of practical value to manufacturers of automobile inner tubes. This belief led to the stretching of the rubber slabs in many of the tests made during the present series of investigations (*11*). Although stretched slabs have

been used before in studies of permeability (*4*, *16*), no data have been presented on the change in permeability with increase in the degree of stretch. Daynes has pointed out that, as a consequence of the difficulty of making accurate measurements of the thickness of stretched membranes, it should be no easy task to obtain accurate data on this effect. Certainly the measurements described herein were not so accurate as most of those made during the study of other phases of the problem.

In one series of tests (made with apparatus A) determinations were made of the permeability of a pure-gum slab, which was subjected to different degrees of stretch (in one direction only) by clamping it between the jaws of the permeameter at zero stretch and subsequently adjusting the distance between the jaws. After the latter had been adjusted to the position desired for each test, the upper chamber, *W*, was brought

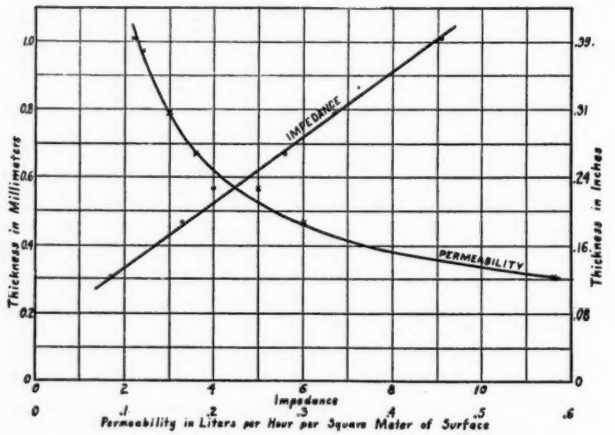

Figure 2—Variation of Permeability with Thickness

down so as to hold the rubber slab tightly against the lower chamber, *U*. The permeabilities corresponding to stretches of 0, 9.8, 19.7, 29.5, and 39.3 per cent were, respectively, 0.25, 0.26, 0.27, 0.28, and 0.29. The increase in permeability for a stretch of 39.3 per cent is thus only 16 per cent. Too great a significance is not to be attached to these values, however, as the permeabilities were determined in every case immediately after the slab had been stretched, and not after an equilibrium condition had been attained.

When this same slab was left stretched 39.3 per cent for several hours, the permeability increased from the 0.29 value given above to 0.31, a total increase in permeability of 24 per cent as compared with that at zero stretch. The rubber apparently undergoes a slow period of adjustment after being stretched. Although the maximum stretch in one direction was 39.3 per cent, the contraction at right angles to stretch

was so pronounced in the case of this thin slab that the measured increase in area as a consequence of stretch was but 14.4 per cent. (This measurement was made from the indentation left on the slab at the line of contact with the air chambers, the indentation being visible for several minutes after removal from the apparatus.) Assuming that the volume remained constant, this increase in area would indicate a decrease in thickness from the measured value of 0.47 mm. to 0.40 mm. By using the previously established relationship between permeability and thickness, it can be calculated that such a change in thickness should result in an increase in permeability from the originally measured value of 0.25 to 0.29. Since the final experimentally determined value was 0.31, it appears possible that stretched rubber is actually more permeable than unstretched rubber. It can be said, however, that most of the increase in permeability resulting from stretch can be accounted for by the decrease in thickness accompanying the stretch. Similar but less complete measurements on another slab of the same stock gave results similar to those reported above, except for one measurement which seemed to be out of line with the others.

Winkelmann and Croakman (*15*) have recently reported data indicating an increase in the absolute quantity of water absorbed as a consequence of stretching the rubber strips under investigation.

In connection with the effect of stretch on permeability the reader is also referred to the section on the "Effect of Compounding Ingredients on Permeability," in which data are shown on the permeabilities of various compounded stocks in the stretched and unstretched conditions.

Variation of Permeability with Nature of Crude Rubber

To what extent the nature of the crude rubber may influence the permeability of vulcanized stocks appears to have received practically no mention in the literature. Hauser (*7*), in the discussion following a paper presented by Daynes (*3*), stated that tests at a certain factory had shown the permeability of "whole rubbers" to be far less than that of "rubbers produced from dough." Since solubility of a gas in rubber is one factor influencing the permeability of the rubber towards the gas, an observation made by Venable and Fuwa (*14*) during an investigation of the solubility of various gases in rubber may be of interest. These investigators found the solubility of carbon dioxide in a sample of unvulcanized pale crepe to be nearly 10 per cent less than in a sample of unvulcanized smoked sheet. Schumacher and Ferguson (*12*) also found the diffusion of water to be considerably faster through vulcanized smoked sheet than through vulcanized pale crepe.

In a direct comparison made in this laboratory, four different rubbers were used—high-grade smoked sheets, first latex crepe, rolled brown crepe, and a wild rubber of the grade marketed as "caucho ball." Each was mixed in a

pure-gum stock of the same nature as the smoked-sheet stock previously described. All stocks were vulcanized for 40 minutes at 300° F. (149° C.). The results obtained with apparatus A under the usual operating conditions are shown in Table II, all values being calculated to an average thickness of test slab of 1.04 mm.

Table II—Variation of Permeability with Kind of Crude Rubber Used in Stock

Kind of Rubber	Permeability of Cured Stock *Liters/hour/sq. m. surface*
Smoked sheets	0.11
First latex crepe	0.11
Rolled brown crepe	0.11
Caucho ball	0.08

These results indicate there is little choice among the commonly used crude rubbers from the point of view of permeability. The caucho ball appears, on the basis of the single

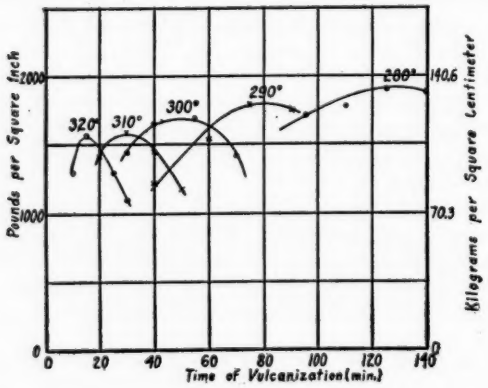

Figure 3—Stress at 600 Per Cent Elongation at Various Temperatures of Vulcanization

stock tested, to offer more resistance to the passage of air than do the plantation rubbers. Since the plantation-rubber stocks were already cured to a state very close to that of minimum permeability, as proved by later experiments on the effect of state of cure, the advantage of the wild-rubber stock cannot be explained on the basis of a different state of cure. Since the caucho ball used was probably a mixture of Hevea and Castilloa rubbers, it seems that a study of the permeability of rubbers obtained from various species of rubber-producing trees might be well worth while.

Some information in regard to the permeability of "whole" rubber (prepared by the spray process) has been obtained in this laboratory.[3] On working with first-grade inner-tube stocks and making measurements with apparatus B, it was observed that the stock made with latex sprayed rubber was about 7 per cent less permeable than the similar stock made

[3] Measurements made by J. W. Liska.

from smoked sheets. Experimental error and differences in the exact state of cure could have accounted for most of this difference. It thus seemed that, if this whole rubber originally possessed the considerable advantage claimed for whole rubbers by Hauser (*7*), it lost nearly all of its superiority upon being milled into a stock.

Some results obtained by the writer on pure-gum stocks made with guayule rubber, which will be presented in detail at a later date, indicated a rather low permeability for the guayule stocks when cured to a state comparable to that of a smoked sheet control. In fact, the permeability seemed to be roughly proportional to the content of rubber hydrocarbon in the guayule rubber. The 20 per cent or more of resinous matter in the guayule rubber deduced its permeability by nearly 20 per cent.

Effect of Milling on Permeability

Kohman (*9*), studying the effect of overmilling on the absorption of oxygen by vulcanized rubber, found that 60 minutes' milling, as compared with the regular milling time of 20 minutes, resulted at first in an increased rate of absorption. The total absorption after standing 600 hours and longer was, however, less for the overmilled than for the control sample. The present writer has found no reference in the literature to any study correlating permeability and milling.

It was thought possible that the study of the effect of milling might cast some light upon the recent theory of the structure of rubber proposed by Hauser (*8*) and others. According to Hauser, the latex particle consists of soft, tacky rubber hydrocarbon surrounded by a tougher outer shell of rubber hydrocarbon and adsorbed protein matter. The latex particle retains its shape, although probably not its exact consistency, after coagulation to form crude rubber. In accordance with this theory, milling crude rubber on a cold mill should break many of these outer shells so that the mass of rubber will be modified considerably. In milling on a hot mill, on the other hand, the higher temperature is said to give to the latex particles a mobility which enables plasticization without rupturing the shells to any great extent. On the basis of this theory, it was thus to be anticipated that, if milling had any effect at all on permeability, hot milling should have much less influence than cold milling.

The study of the effects of hot and of cold milling on permeability was made with apparatus B. The operating temperature was 30° C. and the pressure 46 pounds per square inch (3.23 kg. per sq. cm.). The pure-gum stock used was compounded according to the previously described formula.

Cold Milling—A batch (1180 grams) of the stock was first mixed on the laboratory mill, the total milling time being 15 minutes and the mill being originally as cold as the cold-water cooling system would make it. (The temperature of the inlet water was about 18° C.) A sample was then re-

moved for curing. After the mill had again been cooled to a temperature as low as possible (about 10 minutes required), the batch was returned to the mill, mastication was continued for 10 minutes, and the second sample removed. This procedure was followed until the total milling time was 65 minutes. The test slabs were cured for 30 minutes at 292° F. (144.4° C.). The values shown in Table III have all been corrected to the same slab thickness.

Table III—Effect of Cold Milling on Permeability

Total Milling Time	Permeability
Minutes	*Liters/hour/sq. m. surface*
15	0.23
25	0.22
35	0.21
45	0.21
55	0.21
65	0.21

Unfortunately the earliest effect of milling could not be determined, as some milling was necessary to produce a stock suitable for the initial cure. The results indicate that the sample milled the shortest length of time was the most permeable. Although the difference is not large, it is thought to be a real one and not due to experimental error, since the measurement was repeated three times without uncovering any appreciable error.

Hot Milling—The conditions were the same as those prevailing for cold milling except for the milling process itself. The mill was heated by steam during the latter experiments. The exact temperature of the mill was not measured, however. The first sample was removed after 7 minutes' milling, and the subsequent samples after the intervals indicated in Table IV.

Table IV—Effect of Hot Milling on Permeability

Total Time of Milling	Permeability
Minutes	*Liters/hour/sq. m. surface*
7	0.23
17	0.24
27	0.23
42	0.24

Comparison of Cold and Hot Milling—Although they do not necessarily conflict with other theories, the results can be explained by Hauser's theory of the structure of crude rubber. Hot milling, which presumably does not break up the latex particles in the crude rubber appreciably, had very little effect on the permeability of rubber to air. There is some evidence, on the other hand, that the early stages of cold milling tend to alter the stock in the direction of decreasing permeability. It is conceivable that in the original crude rubber the latex particles are not packed compactly enough to offer the maximum resistance to the passage of gaseous molecules. After breaking up the particles during cold milling, the rubber hydrocarbon becomes the continuous matrix in a stricter sense, and the resistance to the passage of gases becomes greater. Grenquist (*6*) has recently demonstrated by means of photomicrographs made on unvulcanized

samples that progressive milling results in a steady increase in the homogeneity of the matrix.

From the practical point of view, the effect of milling on permeability is relatively insignificant.

Effect of Temperature of Vulcanization on Permeability

Edwards and Pickering (*5*) presented some data on the permeability of samples of balloon fabric vulcanized at different temperatures. Since they made no attempt to conduct comparisons on samples at comparable states of cure (as measured either by physical tests or chemical analyses), their results contribute practically no information regarding the effect of the temperature of vulcanization on permeability.

In the work carried out by the writer for the purpose of establishing the influence of this factor on permeability, it was considered desirable as a preliminary step to determine what lengths of cure at the various temperatures would give comparable states of cure. The time necessary to give maximum stress at an elongation of 600 per cent was the criterion used. For this study a large (1500 grams) batch of the previously mentioned pure-gum stock was mixed on an experimental mill. Portions of this batch were vulcanized for various lengths of time at various temperatures in a paraffin bath. The determinations of stress at 600 per cent elongation were made on the Scott testing machine. The modulus curves plotted from the data obtained are shown in Figure 3. By choosing the maximum modulus in each case, lengths of comparable cure for temperatures of 320°, 310°, 300°, 290°, and 280° F. (160°, 154.4°, 148.9°, 143.3°, and 137.8° C.) were taken as 15, 30, 50, 80, and 130 minutes, respectively. Permeability test slabs were then vulcanized for the designated lengths of time (Table V) at the various temperatures.

Apparatus A was used in making the determinations of permeability. The slabs were stretched 37 per cent in one direction immediately before being tested. The usual conditions with respect to temperature and pressure were maintained. The results (Table V) have all been calculated to a hypothetical thickness of 0.030 inch (0.76 mm.).

Table V—Effect of Temperature of Vulcanization on Permeability

Temperature		Length of Cure	Permeability
° F.	*° C.*	*Minutes*	*Liters/hour/sq. m. surface*
320	160.0	15	0.16
310	154.4	30	0.15
300	148.9	50	0.15
290	143.3	80	0.15
280	137.7	130	0.16

Since the variations in the values for permeability shown in Table V were scarcely outside the limit of experimental error, it may be concluded that the temperature of vulcanization over the range investigated had no appreciable effect on permeability. This conclusion should be of interest from the practical point of view, since there has been in recent years

a pronounced tendency towards shorter cures at higher temperatures in the case of inner-tube stocks.

Effect of Compounding Ingredients on Permeability

There are certain data in the literature relative to the effect of compounding ingredients on the solubility of gases in rubber. Steinitzer (*13*) stated that the absorption of carbon dioxide by compounded rubber stocks was more or less proportional to the rubber actually present. Venable and Fuwa (*14*) reached a similar conclusion after obtaining data indicating that as much as 10 parts of zinc oxide and 17 parts of free sulfur reduced the solubility of carbon dioxide only in proportion to the reduction in the volume of rubber present in the stock.

Most of the published results correlating compounding ingredients and permeability have not been very quantitative in nature. Steinitzer found considerable variation in the permeabilities of tubes containing various quantities of mineral matter. His data indicated no direct relationship, however. After discussing the lack of accurate data on the subject, Daynes (*3*) stated that "Shakespear has found considerable variation in permeability among commercial sheets." Without making any systematic investigation of the matter, Schumacher and Ferguson (*12*) were led to the belief that fillers have little effect on the diffusion of water through thin rubber sheets, except in cases where they alter the hardness of the rubber appreciably.

Davey and Ohya (*1*) studied the permeability of compounded rubber to hydrogen, the rubber mixings being "topped on to cambric by means of a factory calender." The interferometer method (*5*) of measurement was used. The conclusions reached were that (1) accelerators, softeners, and antioxidants reduce permeability; (2) the addition of 10 per cent by volume of carbon black or zinc oxide increases permeability slightly; and (3) the addition of 10 per cent by volume of Dixie clay or whiting increases permeability very markedly.

The initial study of the effect of compounding ingredients made by the writer involved a comparison of the effects of a few of the commonly used fillers or pigments. The pigments were added to the previously described pure-gum compound to the extent of 15 per cent by volume. In the case of zinc oxide the 15 per cent was in addition to the small quantity already present and necessary for vulcanization. The results obtained under the usual operating conditions with apparatus A are shown in Table VI. Two sets of testing slabs were cured for 30 minutes at 300° F. (149° C.), one being tested under a stretch in one direction of 37 per cent and the other being tested in the unstretched condition. All values for permeability appearing in Table VI have been corrected to a thickness of the original slab of 0.69 mm.

Table VI—Effect of 15 Per Cent by Volume of Certain Common Compounding Ingredients on Permeability

Pigment Present	Permeability: Sample stretched 37%	Permeability: Sample not stretched
	Liters/hour/sq. m. surface	
None	0.20	0.16
Zinc oxide	0.16	0.13
Channel black	0.16	0.11
Clay	0.13	0.11
Thermal decomposition black	0.17	0.14
Blanc fixe	0.15	0.12
Whiting	0.17	0.14

Differences in the states of cure of the various stocks undoubtedly had some influence on the results. In studies made on the effect of state of cure on permeability (results to be published later) it was found that stocks of this nature passed through a minimum in permeability as vulcanization is increased. Curing tests indicated the stocks tested above to vary in rate of cure. With one exception, however, the cure actually given (30 minutes at 149° C.) was such as to cause the permeabilities of the stocks to vary from the minimum possible permeability by less than 5 per cent. The slab of the stock containing carbon black was, on the other hand, sufficiently undercured in the permeability test so that its permeability was about 10 per cent greater than would have been the case had its state of cure been comparable to that of the control stock. Carbon black, therefore, deserves a better rating by about 10 per cent than the data shown in Table VI would give it.

In summarizing the tests made on both stretched and unstretched slabs, it seems that the clay and carbon-black stocks were slightly the best, with those containing blanc fixe and zinc oxide following closely. The stocks containing the thermal decomposition carbon and whiting were the poorest. From the practical standpoint blanc fixe, a very commonly used ingredient for inner-tube stocks, was one of the most satisfactory pigments studied.

Table VII—Effect on Permeability of Various Quantities of Zinc Oxide

Volume of Zinc Oxide	Permeability
% on rubber	*Liters/hour/sq. m. surface*
0	0.17
5	0.15
10	0.15
15	0.14
20	0.13

The next project undertaken involved the study of the variation of permeability with variations in the volume of pigment present in the rubber stocks. For this study stocks were mixed containing, in addition to the small percentage necessary for vulcanization, 5, 10, 15, and 20 per cent by volume of a fine zinc oxide made from zinc metal. Test slabs of these stocks, which were found in separate tests to have the same rate of cure, were vulcanized under conditions similar to those of the stocks previously discussed. The results of permeability determinations on unstretched slabs are shown

in Table VII, all values being corrected to a thickness of testing slab of 0.65 mm.

When the stock containing 5 per cent of zinc oxide failed to show a greater permeability than that containing 10 per cent, the measurement was repeated. No difference in permeability was found, however. The value for the pure-gum control stock represents the average of three measurements which checked satisfactorily; a fourth, which indicated a permeability 8 per cent higher, not being used in averaging.

It will be noted that there is a more or less steady decrease in permeability as the volume of pigment is increased. In fact, although the exact relationship cannot be stated, it appears that the reduction in permeability is roughly proportional to the increase in volume of pigment present.

The last study undertaken in connection with compounding ingredients was that involving the incorporation of a large number of various agents, most of which were softeners or other organic substances. Since the quantities added were governed somewhat by the nature of the materials involved, the results are not comparable in a quantitative sense. It was merely hoped that if any of these materials was capable of reducing permeability appreciably, that material would appear to sufficient advantage to distinguish it from the others. The results of tests carried out under the same conditions as for the other tests reported in this section are shown in Table VIII. The values for permeability are all corrected to a thickness of testing slab of 0.76 mm.

Table VIII—Effect of Various Compounding Ingredients on the Permeability of Rubber Stocks

Compounding Ingredient	% (by wt.) on rubber	Permeability Liters/hour/sq. m. surface
Glue	33	0.10
Vaseline	10	0.15
Rosin oil	10	0.13
Pine oil	10	0.17
Turpentine	10	0.14
Asphalt	10	0.13
Pine tar	10	0.15
Candelilla wax	5	0.15
Stearic acid	10	0.14
Linseed oil	10	0.17
Paraffin wax	1.5	0.16
Cottonseed oil	10	0.16
Mineral oil	10	0.13
Castor oil	2.3	0.14
Glycerol	1.8	0.16
Ivory soap	6.7	0.21
Sodium silicate	10	0.18
None		0.14

In no case was any unusual reduction in permeability obtained. The reduction attributable to the incorporation of 33 per cent (by weight) of glue was only roughly proportional to the reduction in the volume of rubber present in the stock. In three other cases there was a minor reduction in permeability, while the other thirteen stocks were either approximately equal to or more permeable than the control stock.

It is at once apparent that certain of the results obtained lead to conclusions quite contradictory to those of Davey and Ohya (*1*). These authors reported, for instance, that 5 per cent of softeners (kind not stated) reduced permeability by 50 per cent in cured stocks and nearly 40 per cent in uncured stocks. None of the various softeners tested by the writer had any appreciable effect in reducing permeability, and some of them were rather distinctly disadvantageous. Davey and Ohya found, furthermore, that the incorporation of 10 per cent by volume of zinc oxide, carbon black, Dixie clay, or whiting increased permeability, whereas in the present work it was discovered that 15 per cent by volume of these pigments reduced permeability. In considering these discrepancies, attention should be directed to the fact that Davey and Ohya were using hydrogen instead of air, were working at atmospheric pressure rather than with a pressure difference of more than 3 atmospheres, and were using thin rubber membranes "topped on to cambric." They assumed that the canvas offered no resistance to the passage of gas, since the rubber did not enter the canvas. The fact that several investigators (*3*, *5*) have found the permeability of rubber applied as proofing on balloon fabric to be markedly affected by the fabric renders this assumption somewhat open to question. In regard to the effect of pigments, it is conceivable that aggregates of these could have produced localized regions of reduced thickness to such an extent as to increase permeability. Such a condition might exist much more readily in the case of the thin membranes (0.1 mm.) used by Davey and Ohya than the thicker ones (0.7 mm.) employed by the writer.

From the various tests reported in this section, therefore, it appears that, as far as the inherent permeability of the rubber itself is concerned, little is to be accomplished by the incorporation on the mill of various compounding ingredients. The reduction in permeability is in no case appreciably greater than that resulting from the reduction in the volume of rubber present in unit volume of the stock.

Summary and Practical Conclusions

The permeability of rubber membranes was found to be approximately inversely proportional to thickness. The recently developed "super" automobile inner tubes are therefore undoubtedly better air containers than the ordinary tubes of smaller gage.

Most of the increase in permeability resulting from stretch can be accounted for by the decrease in thickness accompanying stretch.

Pure-gum stocks made from various commonly used plantation rubbers did not vary much in permeability. A stock made from a wild rubber, caucho ball, had a somewhat lower permeability.

Milling on a steam-heated mill was found not to change permeability appreciably. The early stages of milling on a cold mill reduced the permeability of a stock slightly.

The temperature of vulcanization seemed to have no influence on permeability, provided the test slabs were cured to the same state. It may be concluded, therefore, that the recent trend towards higher temperatures of cure for inner tubes has not adversely affected their air-retaining capacities.

None of the various softeners or other organic materials tried was found to effect any appreciable decrease in the permeability of a rubber stock.

The results indicate that permeability is roughly proportional to the volume of rubber hydrocarbon present in a stock. The nature of the principal compounding ingredient used in a stock does have some influence on permeability, however. Clay, channel black, and blanc fixe are among the compounding ingredients having the most beneficial influence on permeability.

Experiments with stocks containing various quantities of zinc oxide indicate that permeability varies inversely with the volume of pigment present. From the standpoint of the air-retaining capacity, the loading of inner-tube stocks with pigments is therefore desirable.

Acknowledgment

Certain contributions to this investigation made by J. W. Liska, have already been mentioned. The writer wishes also to acknowledge his indebtedness to Mr. Liska for assistance in the experiments involving the effect of milling on permeability. Acknowledgment is also gladly given to J. N. Street and N. A. Shepard for their many suggestions and willing counsel throughout the course of this investigation.

Literature Cited

(1) Davey and Ohya, *Trans. Inst. Rubber Ind.*, **5**, 27 (1929).
(2) Daynes, *Proc. Roy. Soc.* (*London*), **97A**, 286 (1920).
(3) Daynes, *Trans. Inst. Rubber Ind.*, **3**, 428 (1928).
(4) Dewar, *Proc. Roy. Inst. Gt. Britain*, **21**, 813 (1915).
(5) Edwards and Pickering, Bur. Standards, *Tech. Bull.* **387** (1920).
(6) Grenquist, IND. ENG. CHEM., **22**, 759 (1930).
(7) Hauser, *Trans. Inst. Rubber Ind.*, **3**, 451 (1928).
(8) Hauser, "Colloid Chemistry of the Rubber Industry," p. 33, Oxford University Press, 1928.
(9) Kohman, *J. Phys., Chem.*, **33**, 226 (1929).
(10) Lambourn, *Trans. Inst. Rubber Ind.*, **3**, 452 (1928).
(11) Morris and Street, IND. ENG. CHEM., **21**, 1215 (1929); *India Rubber J.*, **79**, 25 (1930).
(12) Schumacher and Ferguson, IND. ENG. CHEM., **21**, 158 (1929).
(13) Steinitzer, *Gummi-Ztg.*, **26**, 1626 (1912).
(14) Venable and Fuwa, J. IND. ENG. CHEM., **14**, 139 (1922).
(15) Winkelmann and Croakman, private communication.
(16) Wroblewski, *Pogg. Ann.*, **158**, 539 (1876).

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New Autographic Machine for Testing Tensile Properties of Rubber[1]

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A description is given of a testing machine for the measurement of the tensile strength of materials having considerable deformation, such as rubber.

A stress-strain recording device is described in which the strain recorded responds to the separation between a pair of independently movable pointers which may be made to follow the separation of two marks, spaced upon the sample before insertion in the machine.

Mechanical means are also described to correct for variations in the test-piece cross section, and to produce equal chart displacements for equal angular deviations of the inclination balance.

MACHINES have been devised heretofore for determining the per cent elongation of rubber with application of load, but such machines are open to criticism because of calculations required and the personal error involved in determining the elongation.

Identified with this subject, as recorded in the literature, we find such names as Breuil, 1907 (*2*), Schopper and Dalen, 1909 (*8*), Beadle and Stevens, 1909 (*1*), Schwartz, 1910 (*9*), Olsen, 1910 (*6*), Cheneveau and Heim, 1912 (*4*), Scott, Cooey, and Burkley, 1922 (*3*), Depew, 1922 (*5*), Schob, 1923 (*7*), and Williams, 1925 (*10*).

The machine herein described, as designed by the author, aims to avoid the criticisms above mentioned by embodying a recording device so operated as to provide mechanically a

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stress-strain curve upon ordinary coördinate paper, giving the desired results in a form which can be directly used for record.

Referring to the photographs and sketches, Figure 1 represents a general view of the machine and illustrates with some detail the following parts: *L*, pendulum-lifting arrangement; *S*, scales on which are directly indicated the settings of the weight lifter for the different gages of the test pieces; *A*, arcuated member to which is trained the cord connecting the pendulum displacement with the horizontally moving plate of the charting arrangement.

This photograph shows a general view of the machine as in use at the different Goodyear plants.

A favorable comparison with any other standard machine

Figure 1—General View of Machine

is obtained when the following features are considered: (1) the comparatively high speed of performance (25 tests and more per hour); (2) the accuracy of results; (3) the duplicability obtained by mechanical means in preference to visual observation.

No calculations are required and the records obtained can be used directly for the measurement of the area under the stress-strain curve or for any other purpose.

Figure 2 is intended to illustrate the following devices: *C*, the type of clamps used to hold the test piece in position; *R*, the alignment rollers used to counteract the tendency of the rubber to slip from the clamps on account of the lifting action of the pointers of the two elongation carriages; *F*, the two followers or carriages following the two bench marks at the reduced portion of the test piece; *D*, the type of device used to engage or disengage the clamp carriage at the right, from the rotating driving screw; *W*, the method of driving the chart-supporting plate by means of a counter-

balancing weight, in response to the pendulum movement; and *P* the type of pen support and the guides along which the small pen carriage is raised or lowered by the lengthening or shortening of the distance between the two carriages following the two bench marks.

Figure 3 represents diagrammatically the fundamental principles on which the performance of the machine is based. The sketch also illustrates the linking of the different parts and the coördination of the movement of the chart with the movement of the pen, to produce the curve representing the stress-strain relationship. As indicated at the left, the force-measuring device is a modified pendulum balance. The weights operate in a slot and can be raised or lowered to decrease or to increase the length of the operating arm. At the center of the pendulum, secured to the shaft, is illustrated the type of cam used to maintain such a rate of loading as to produce, on the chart, equal spacing for equal angular devia-

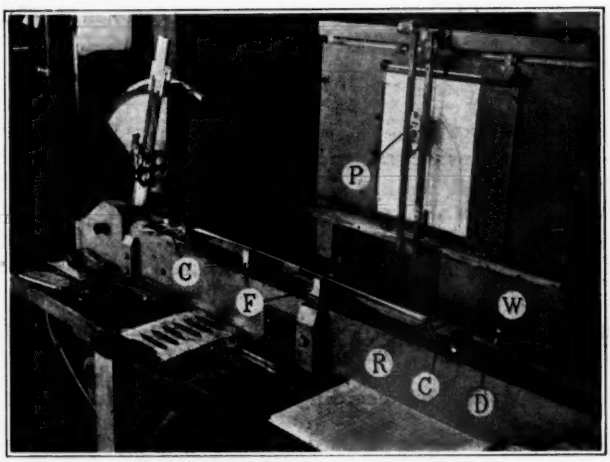

Figure 2—Machine with Test Piece in Place

tions of the pendulum. At the center of the sketch is shown the method of recording the load and the method of transmitting to the recording pen the separation between marks. A slight tension of the cord interconnecting the movable members of the elongation system is effected by the small weight of the pen carriage. The method of obtaining the vertical line expressing the ultimate load is also obtained by the indirect action of the weight of the pen carriage. In fact, this will drive together the two followers as soon as the test piece breaks, and therefore as soon as the points of the two followers are released from their hold against the rubber sample.

Figure 4 shows on the same chart the stress-strain curves obtained by three typical factory stocks: a tread stock, a carcass stock, and a truck-tube stock. In this chart the

load is expressed in pounds per square inch. The curves are, however, generally recorded in charts expressing the load in kilograms per square centimeter. The two types of charts are so designed as to make the readings interchangeable. As shown in Figure 4, the straight lines parallel to the elongation axis determine with the load axis the ultimate load of the test pieces.

Figure 5 represents a somewhat more detailed view of the machine. The sketch is somewhat schematic, the purpose being to emphasize the interconnection of the different moving members. The front rail is removed so as to show the clamp carriages, the construction of the followers, the method of

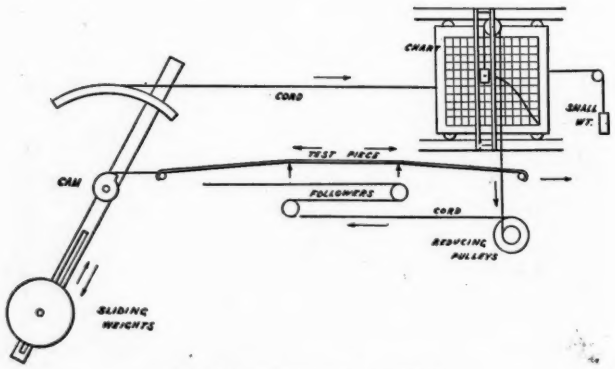

Figure 3—Diagram of Machine

operation of the small pulleys supported by the followers, the reducing pulleys, and other important parts.

Method of Recording Stress-Strain Data

In the following is outlined a detailed description of the most important parts of the machine, and their performance in coördination with each other, to produce the stress-strain curve.

Weighing Mechanism—A lever, 1 (Figure 5), is pivotally mounted upon one end of the table 2, adjacent to the carriage guides, 3 and 4 (Figure 8). The lever (Figures 6 and 7) is constructed of a top portion, 5, provided with a rack, and a lower portion, 6, having an elongated slot whereby a weight or set of weights can be secured at different positions on the lower part of the lever. In order to have means for maintaining the lever in position advanced from the vertical, it is provided with pawls mounted upon its lower end, 8. The pawls are normally engaged with a rack, 9 (Figure 5), secured to the table, but means are provided for holding the pawls out of engagement whenever required.

A bracket, 10 (Figure 7), is secured to the lever and supports an arcuated grooved member, 11 (Figure 6). To this

arcuated member is trained a cord, 12 (Figure 5), transmitting the motion of the weighing device to the recording mechanism.

COMPENSATION FOR GAGE VARIATIONS OF TEST PIECES—In order to obtain an accurate comparison between different test pieces of the same width but of different gage, the adjusting device, 13, is utilized. This device is raised or lowered by first raising the pin, 14, at the end of the lever, 15, from engagement with the wheel, 16, perforated at the edge, and then by turning the knurled wheel, 17, to operate the rack and pinion, 18 and 19. The adjusting device is rigidly connected by means of two lateral bridles to a cross-shaped piece supporting the weights, 7. By this arrangement it is possible to raise or lower the pendulum weights with small effort and with rapidity in setting.

It is obviously possible to take care of practically any reasonable variation of gage, the only limitations being an

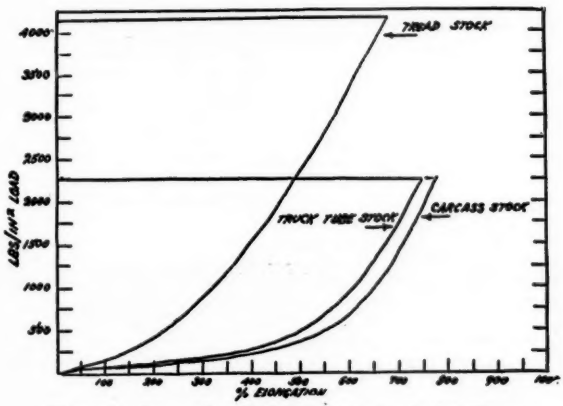

Figure 4—Stress-Strain Curves Obtained with Three Factory Stocks

excessive weight or an excessive length of moment arm. In the latest machines use is made of three sets of weights, making possible the testing of samples in a range of thicknesses from 0.95 to 3.40 mm.

There are three scales, each related to one of the three sets of weights, and to a definite group of gage variations. The gage of the test piece is indicated in the corresponding scale and to these positions is lifted or lowered the weight-lifting device, 13.

CAM MEMBER—The cam member, 20, is mounted upon the pendulum lever to serve as a connection, together with a steel ribbon or a small sprocket chain, to one of the two carriages to which the test piece is clamped. The cam member is designed according to a curve calculated to compensate for the proportionally decreasing acting leverage of the pendulum weight with the increase of the pendulum displacement. In calculating the cam shape, account is also taken of the action of the counterbalance weight, 28.

As the pendulum lever, 6, is displaced from the vertical, the moment arm of the test piece is continuously changed so that the load is in every instance proportional to the distance traversed by any point of the arcuated member, 11. Equal increments of load are therefore made directly proportional to equal angular displacements of the pendulum from the vertical.

CHARTING LOAD—A recording device is mounted upon a frame, 21, which is supported by the guide member, 3. A plate, 22, is mounted upon a number of rollers, 23, which ride in channels of the frame. A cord, 12, is connected at one end, by means of a small regulating drum, 24, to the plate, trained over the grooved member, 11, and connected thereto by means of an adjustable thumb screw, 25. Another cord, 26, connected to the moving plate, is trained over a pulley, 27, mounted upon the frame, and is secured to a weight, 28, by the other end. Two guides, 29, are mounted upon the frame to provide a support for a member, 30, that carries a tracing

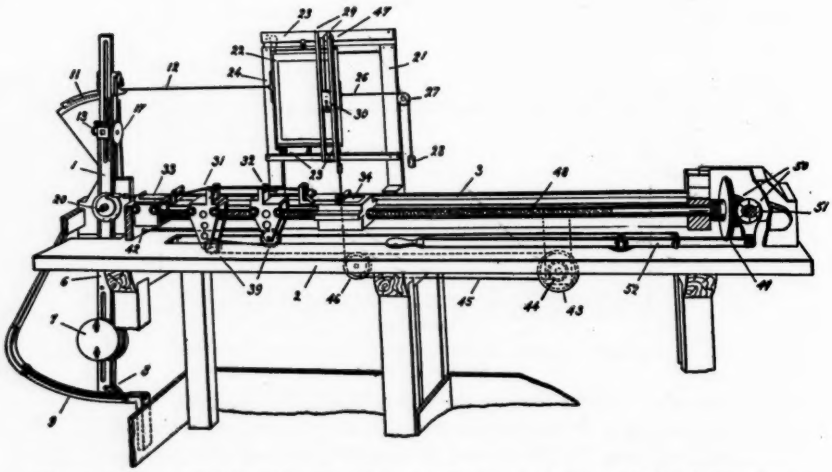

Figure 5—Sketch of Machine Emphasizing Interconnection of Moving Members

pen. The pen may be moved into and out of contact with the plate, and therefore with the coördinate paper mounted thereon.

CHARTING ELONGATION—The most important parts of the elongation charting system are the elongation carriages, 31 and 32 (Figures 5 and 8), operating between the carriage, 33, and the sliding member, 34, which are supporting the clamping devices at the two ends of the test piece. These members, 31 and 32, are similar in construction, each having rollers mounted upon the sides and so adjusted as to ride in the channels, 36, of the guides. They also have two lower arms, 37 (Figure 9), which carry a shaft, 38, upon which a pulley, 39, is freely mounted. A V-shaped member,

40, is mounted in a recess in the top of both members, supporting a centrally located pointer, 41. These pointers have a shank set within a spring and exert a slight pressure on the test piece.

The two members 31 and 32 differ in construction in

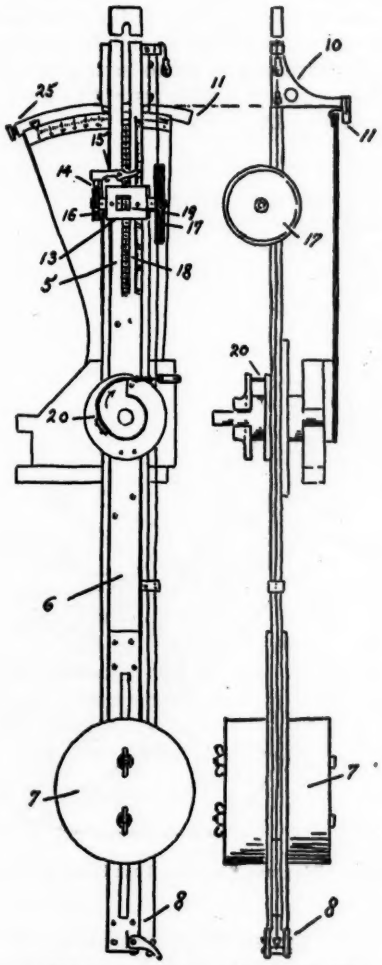

Figure 6—Front View of Weighing Mechanism

Figure 7—Side View of Weighing Mechanism

that the arms of the member 31 are somewhat longer than those of the member 32, in order to stagger the pulleys with respect to each other. The members 31 and 32 are connected together and are interconnected to the member 30 by means of a system of two cords.

A cord secured at the left end to the table, 42, is trained

first over the pulley of the follower 32 at the right, next over the one of the follower at the left, 31, then wrapped once or twice over the largest of the two reducing pulleys, 43. A second cord, 45, first secured and wrapped once over the smallest of the two reducing pulleys, 44, is trained over a pulley, 46, mounted upon the table, 2, then over the small idler at top of the pen-carriage guides, and finally is fastened to the pen carriage. The two pulleys 43 and 44 are utilized to provide a reduction system, so as to secure proper length of movement of the member 30 with respect to the separation of the carriages 31 and 32.

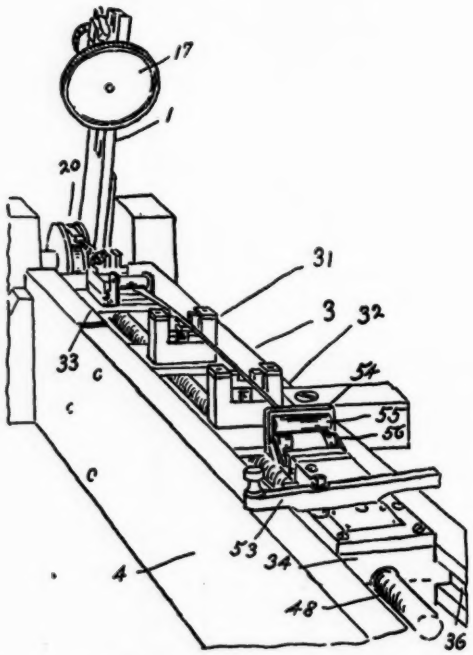

Figure 8—Diagram Showing Test Piece in Position

STRAINING MECHANISM—This mechanism, as represented in Figure 5, illustrates the original type constructed, which was designed both for tensile tests and for the study of the hysteresis of rubber compounds. In the machine as illustrated in Figures 1 and 2, the straining mechanism is simplified and designed to provide only one direction of motion.

The mechanism, as represented in Figure 5, consists of a number of movable members mounted between two guides, of which only the rear one, 3, is shown. A longitudinally extending threaded shaft, 48, is mounted between the two guide members and is driven through the agency of a bevel

gear, 49, mounted upon one end. This gear is driven by pinions, 50, mounted on a shaft connected to a lever, 52, whereby these pinions may be moved into and out of engagement. Any suitable means may be employed for driving the shaft, 51, such as a motor belted to it. A carriage, 34, is mounted upon the shaft (Figure 8), having an internally threaded portion adapted for engagement with the threaded shaft or disengagement by means of a lever, 53, mounted upon the carriage. The carriage is provided with flanges to fit into the channels of the guides. To the carriage is attached a clamping device including a yoke, 54, which carries a roller, 55, coöperating with the roller 56, to secure the test piece to the carriage. The speed of jaw separation used for testing is 30 inches per minute, but provision is made to operate at 20 inches per minute whenever required.

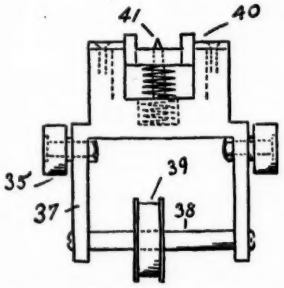

Figure 9—Diagram of Follower Mechanism

Operation of Machine

The operation of the machine is apparent from the preceding description.

The type of test piece used is the ordinary dumbbell, 1 cm. being the width of the reduced portion. Marks at a definite distance are made on the narrower part.

The test piece is secured at one end to the clamping device of the carriages, 33 (Figures 5 and 8), attached to the inclination balance. Bridging over the pointers of the elongation carriages, the other end is clamped to the sliding member 34. The plate is adjusted by means of the small drum in such a position that the tracing device moves on the ordinate, passing through the value zero of the abscissa, when the pendulum is in the vertical position. The carriages 31 and 32, drawn in contact by the weight of the member 30, are dimensioned in such a way that the corresponding pointers are at the same distance as the distance between marks. During the initial elongation of the test piece these pointers are set to correspond with the marks, no further attention being required after the first few inches of stretch. Further, since the carriages 31 and 32 follow the separation of the marks, the tracing pen moves proportionally along the ordinates of the coördinate paper.

In reference to the load, when the pendulum lever is moved in response to the stretching of the test piece, the weight is permitted to draw the plate along its support, whereby normal movement of the plate with respect to the tracing device results. A curve is thus traced which provides a record showing the relation between the load imposed and the resulting elongation.

Acknowledgment

The author desires to express his appreciation for the valuable suggestions and criticism offered by W. W. Vogt during the development of the machine.

Literature Cited

(1) Beadle and Stevens, *J. Soc. Chem. Ind.*, **28**, 1111 (1909).
(2) Breuil, *Caoutchouc & gutta-percha*, **4** (1907); "India Rubber and Gutta-percha," pp. 250–257, Scott, Greenwood, 1910.
(3) Burkley, *India Rubber World*, **67**, 24 (1922).
(4) Cheneveau and Heim, *J. phys.*, **2** (5), 535–50 (1912); *Caoutchouc & gutta-percha*, **11**, 8429–8432 (1914).
(5) Depew, *India Rubber World*, **67**, 154 (1922).
(6) Olsen, *Proc. Am. Soc. Testing Materials*, **10**, 588–91 (1910).
(7) Schob, *Gummi-Ztg.*, **37**, 235 (1923).
(8) Schopper and Dalen, "Lectures on India Rubber," pp. 289–293 (1908).
(9) Schwartz, *J. Inst. Elec. Eng.*, **44**, 693–752 (1910).
(10) Williams, *India Rubber World*, **72**, 411 (1925).

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Microturbidimeter for Determination of Rubber Content of Latex[1]

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It is desirable to devise a method for determining the dry rubber content of latex which will be both more rapid than the two trial coagulation methods and more precise than the hydrometric method. The turbidity of latex, depending upon the volumetric number and size of the suspended rubber particles, offers a satisfactory criterion for the determination of the rubber content of latex. A microturbidimeter, herein described, has been adapted to such determinations. It permits more rapid determinations of the rubber content than the two trial coagulation methods. Its precision is less than the lengthy trial coagulation method, involving coagulation, creping, and drying, but is probably greater than that of the shortened trial coagulation method involving only coagulation and creping. Its precision is approximately 1 per cent rubber in 35 per cent latex.

The turbidity of latex obeys the turbidity-dilution law for rubber-content values less than 15 per cent.

The use of color filters, transmitting the shorter wave lengths of light, minimizes the effects of a difference in the effective mean particle size of different kinds of latex.

LATEX, from which crude rubber is obtained by coagulation, is a white colloidal suspension of the consistency of thick cream. It consists of rubber particles of various sizes suspended in a clear straw-colored serum. The actual

[1] Received April 6, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

distribution of the particle sizes, which range usually from 0.5 to 2.0 microns, differs somewhat for samples from different sources. Although the rubber content of latex from different trees may vary considerably, 35 per cent rubber by weight may be considered a representative figure for the dry rubber content of plantation latex, collected and bulked from a large number of trees.

It is very desirable to know the rubber content of latex to facilitate its proper coagulation and to secure some uniformity in the properties of the resulting crude rubber. Since considerable latex is purchased by the crude rubber producers from various plantations, an accurate knowledge of the rubber content of purchased latex is desirable to establish a fair purchase price for the same. There are in general four methods, either in use or proposed, for the determination of the rubber content of latex—namely, trial coagulation, hydrometric, viscosimetric, and nephelometric.

Trial coagulation is the standard precision method consisting of rapid coagulation of a known amount of latex and subsequent creping, drying, and weighing of the resulting rubber. This somewhat lengthy method may be shortened with a resulting loss in precision by omitting the final drying of the creped rubber and applying an arbitrary correction for the water content of the creped rubber. The hydrometric method, using laticometers, has been subjected to considerable experimentation and has had rather wide adoption. However, this type of instrument has been found by many experimenters to give unreliable rubber determinations. The viscosity of either natural or treated latex has also been found to be an unreliable criterion for the determination of rubber content. Nephelometric methods, one of which has been suggested by Whitby (*4*), have not been fully developed and put into general practice.

Nephelometric or turbidimetric methods offer a most promising field for future development of rapid and precise determinations of rubber content. Ordinary nephelometers and turbidimeters cannot be used for the measurement of natural or moderately diluted latex because of its high turbidity. A supersensitive turbidimeter, the microturbidimeter developed and described by Conklin (*1*), for the measurement of photographic emulsions, has been slightly modified and adapted to the measurement of the rubber content of latex. Its operation is based on the extinction or obscuring of an incandescent filament by a thin film of latex contained between the spherical surface of a convex lens and a flat glass plate.

Theory

If an incandescent filament is viewed through a turbid suspension such as latex, the filament appears yellowish surrounded by a field of less intense diffuse light. As the depth of the suspension is increased, the filament becomes redder

and less intense with respect to the diffuse field and disappears when the two light intensities become approximately the same. The depth of the suspension for this apparent extinction of the filament depends upon the turbidity of the suspension, which in turn depends upon the mean size and volumetric number of the suspended particles, the effective mean wave length or color of the light from the filament, and the refractive indices of the two phases of the suspension. Since the rubber content of the latex depends upon the size and volumetric number of the rubber particles, this extinction principle for turbid suspensions can be used with proper precautions to determine the rubber content of either natural or concentrated latex.

For suspensions, where the concentration only is varied,

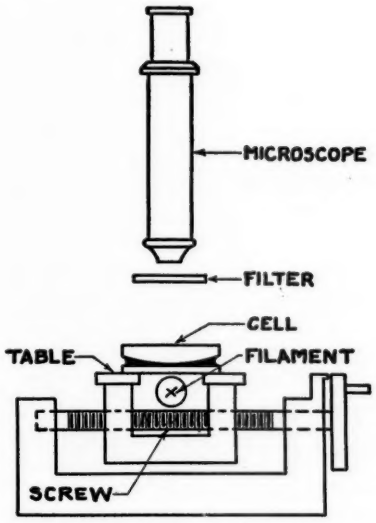


Figure 1—Microturbidimeter

the product of the concentration and the extinction depth is approximately constant—i. e., a curve plotted between the extinction depth and the reciprocal of the concentration should be an approximately straight line. Wells (*3*) gives a fuller discussion of the theory of turbidity.

Instrument Used

The microturbidimeter, shown diagrammatically in Figure 1 and as constructed for plantation use in Figures 2 and 3, consists of a microscope comparator with a traveling table moved by a micrometer screw, an extinction cell containing the sample of latex, and the incandescent filament of a nonfocusing flashlight bulb operated at 1.5 volts. The extinction cell, used during most of the experimental work, consists of a small quantity of latex between the convex surface

of a lens of 8.636 cm. radius of curvature and a flat glass plate. It is shown diagrammatically in Figure 4 and by photograph in Figures 2 and 3. An extinction cell using a glass biprism, with the apex flattened and having a section as shown in Figure 4, was also used. The angle of each half of this biprism is 1 degree 15 minutes.

In the experimental instrument it was possible to interpose color filters between the extinction cell and the viewing microscope. In the plantation latexometer a flat Corning glass filter, known as Sextant Green, was used as the flat plate of the extinction cell. No color filter was used for the data reported on the following curve sheets unless noted otherwise on the sheets themselves.

Figure 2 shows the viewing microscope, *M;* the extinction cell, *C*, in position on the traveling table of the compara-

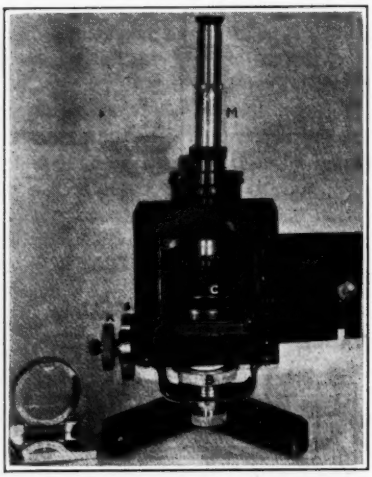


Figure 2—Microturbidimeter Constructed for Plantation Use

tor; the circular scale, *S*, and the knurled heads, *K*, of the micrometer screw; the base, *B*, on which the 3.8-volt flashlight bulb is mounted; and a partially opened extinction cell beside the instrument. Figure 3 shows a fully opened, and also a closed extinction cell containing latex. The dark central spot within the patch of latex of the closed cell represents a clear central spot where the lens rests in contact with the flat glass plate.

Test Samples of Latex

This investigation was restricted to the study of six samples of either preserved plantation latex or commercially concentrated latex because of our remoteness from the sources of natural latex. Two of the six samples were ammonia-preserved plantation latex received in two different ship-

ments of commercial latex. One sample of considerable age, whose exact history is unknown, had apparently concentrated in some manner to a dry rubber content[2] of 44.51 per cent during its storage in the laboratory. This concentration was probably the result of some creaming and the frequent withdrawals of samples of latex from the container. The other was a fresher sample with a dry rubber content of 37.15 per cent. The two samples of commercially concentrated latex listed as Jatex[3] were obtained from the same shipment of Jatex received from Jeavons Tinto & Company of London. Their dry rubber contents were 60.05 and 60.50 per cent, respectively. The two remaining samples of commercially concentrated latex listed as Revertex[4] were obtained from two different shipments of Revertex from the K. D. P. Co., Ltd. One of these samples of Revertex had

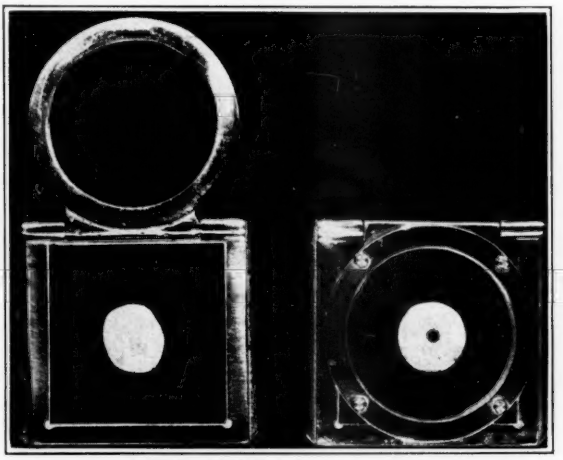


Figure 3—Extinction Cells Containing Latex
Left, fully opened cell Right, closed cell

been previously diluted to a dry rubber content of 52.44 per cent from approximately 80 per cent. The other sample was undiluted with a dry rubber content of 80.0 per cent.

Experimental Procedure

The extinction cell containing latex was placed on the traveling table of the instrument with the light bulb fixed directly under the extinction cell in the field of view of the microscope. The depth, D, of the optical path through the latex within the cell was varied by rotating the micrometer screw and thus shifting the cell sidewise until extinction of the light filament in the microscope field was ob-

[2] The term "dry rubber content of latex" is used to designate the rubber content determined by coagulation, creping, and drying.
[3] Concentrated in a supercentrifuge by the Utermark process.
[4] Concentrated by evaporation.

tained at A and also at B on both sides of the clear central spot of the cell at O (see Figure 4). The extinction width, W, for this combination of latex and cell was obtained from the two micrometer readings corresponding to extinctions at A and B. For theoretical consideration, the extinction depth, D, was computed from the extinction width, W, by the approximate formula

$$D = \frac{W^2}{8R}$$

where R is the radius of curvature of the lens.

Extinction or calibration curves were obtained by observing either extinction depths or widths for different known dilutions of latex of known dry rubber content, and by plotting depths or widths as a function of the rubber content

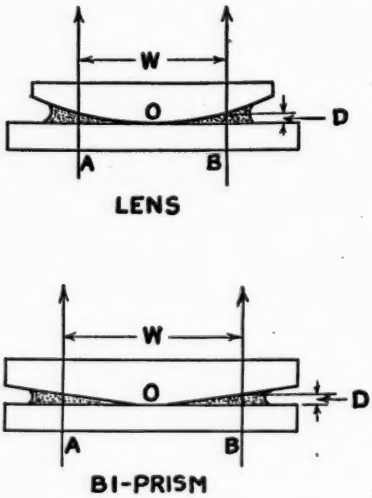


Figure 4—Extinction Cells

O, clear central spot
A and *B*, extinction points
W, extinction widths
D, extinction depths

of the diluted latex. In all of the data shown below, distilled water was used as diluent except where noted otherwise.

Discussion of Extinction and Calibration Curves

Numerous curves, plotted either as extinction or calibration curves, are shown and discussed to give some of the turbid properties of latex and the characteristics of this instrument as applied to latexometry.

Figure 5 gives extinction curves for Revertex using the lens and also the biprism in the extinction cell. These curves are characteristic of the curves for the other samples of latex.

The extreme turbidity of latex is indicated by the fact that films of plantation latex thicker than 0.05 mm. completely obscure the incandescent filament. Extinction cells made of either a lens or the special biprism give closely comparable results. Although the geometry of the cell using the biprism is somewhat simpler than that containing the lens, the lens type of cell has been adopted because of its simplicity and convenience in practice and its easy procurability.

The straight-line portion of the curve of Figure 6, showing the relation between extinction depths and reciprocals of rubber content, indicates that the turbidity of water-diluted latex obeys the concentration-turbidity law when the rubber content does not exceed 15 per cent. This straight-line relation holds for concentrations as low as 0.002 per cent rubber content as measured with a turbidimeter using long columns of highly diluted latex.

Table I—Refractive Indices of Latex and Diluents

Material	Refractive Index
Crude rubber	1.535
Latex serum	1.341
Distilled water	1.333
Glycerol	1.474

Tolman and Vleit (*2*) have observed with a tyndallmeter a phenomenon similar to the minimum of the curves of Figure 5, or the departure from the straight line of Figure 6. No complete or satisfactory explanation of this phenomenon is offered at this time. It is possible that we are concerned with a transition from the transparent phase of water and serum to the partially transparent phase of rubber.

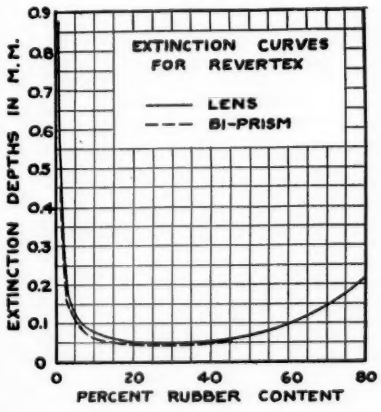


Figure 5

The curves of Figure 7 show the change in the character of the extinction curves when latex serum or glycerol is used as a diluent for latex instead of water. The use of latex serum as diluent does not eliminate the minimum in the extinction curves, but gives an extinction curve very similar to that obtained with water as diluent. Although the use of glycerol as diluent eliminates this minimum, its use as a diluent has no immediate practical value in latexometry, but may have some theoretical interest. It is interesting to

note in Table I the refractive indices of the component phases of latex and these diluents.

The slight difference in the extinction curves for water-diluted and serum-diluted latex is consistent with the slight difference in the refractive indices of water and serum. The great difference in the extinction curves for water-diluted

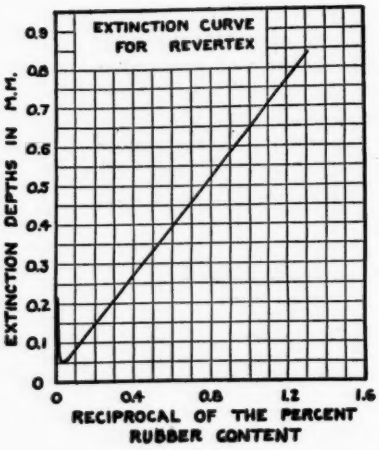
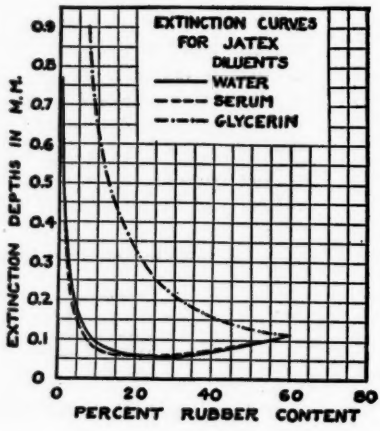

EXTINCTION CURVE FOR REVERTEX
EXTINCTION DEPTHS IN M.M.
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
0 0.4 0.8 1.2 1.6
RECIPROCAL OF THE PERCENT RUBBER CONTENT

Figure 6



Figuer 7

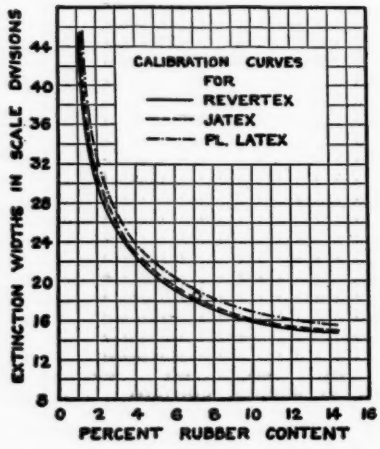

CALIBRATION CURVES FOR
REVERTEX
JATEX
PL. LATEX
EXTINCTION WIDTHS IN SCALE DIVISIONS
8 12 16 20 24 28 32 36 40 44
0 2 4 6 8 10 12 14 16
PERCENT RUBBER CONTENT

Figure 8

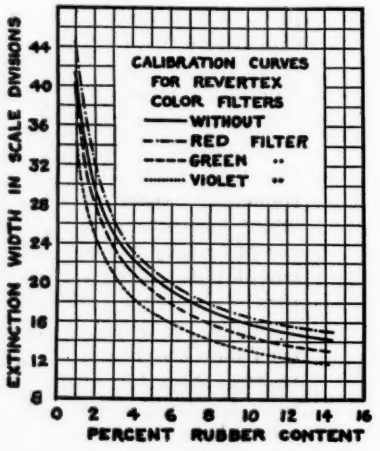

CALIBRATION CURVES FOR REVERTEX COLOR FILTERS
WITHOUT
RED FILTER
GREEN ..
VIOLET ..
EXTINCTION WIDTH IN SCALE DIVISIONS
8 12 16 20 24 28 32 36 40 44
0 2 4 6 8 10 12 14 16
PERCENT RUBBER CONTENT

Figure 9

and glycerol-diluted latex—i. e., the large decrease in the turbidity of the glycerol-diluted latex—is no doubt due to the large increase in the refractive index of the glycerol-diluted serum to a value near that of the suspended rubber.

The rubber content of natural or plantation latex falls in the region of the minimum of the extinction curve where

two values of the rubber content correspond to a single value of the extinction depth. This would result in an ambiguity in converting values of extinction depth into rubber content, if this region of the extinction curve should be used as a calibration curve for the instrument. To avoid this ambiguity, it is desirable to use a moderate, known dilution of the unknown latex, such as a one-tenth dilution of plantation latex. It is then possible to use curves plotted between extinction widths in micrometer-scale divisions and per cent rubber content up to 10 to 14 per cent as calibration curves for the instrument as a latexometer.

Figure 8 shows the calibration curves for the two samples each of plantation latex, Revertex, and Jatex. The two samples of each type of latex—namely, Revertex, Jatex, and plantation latex—give practically identical calibration curves. The calibration curves for these six samples are therefore shown as one curve for each type of latex. The observed differences in the three calibration curves are probably due to differences in the effective mean particle size in these various types of latex—namely, natural and the two types of concentrated latex. Considerable error may be introduced in determining the rubber content of a sample of latex with an incandescent filament alone, unless a calibration curve is used for approximately the same particle-size distribution.

Since the turbidity of latex depends upon the particle size and the color of the transmitted light, it is possible to use filters to minimize this effect of particle size. Figure 9 shows the calibration curves for Revertex obtained with and without color filters. The color filters used were Wratten light filters listed as Orange Red 71 Aβ; Green (Micro-Standard Tricolor) 58 BZ; Violet 76 θ. None of these filters transmitted monochromatic light. The green and violet filters transmitted considerable red which was especially noticeable when the cell was near the extinction point. Latex becomes more turbid with less differences in its extinction owing to differences in particle size as the wave length of the transmitted light decreases.

The green filter is recommended for use in the determination of the rubber content of latex since it is more pleasing to the observer, yields a more sensitive balance than the other two filters, and decreases the spread between the calibration curves for different latices. Figures 10 and 11, giving the calibration curves for Revertex and plantation latex, obtained with and without the green filter, show this decrease in the spread of the two calibration curves. For example, let us assume that a sample of latex is submitted for test. The sample is diluted one part in ten with water and extinction widths of 24 and 22 scale divisions are observed, respectively, with and without the green filter. Without the filter, the calibration curves with a simple multiplication of 10 would indicate a rubber content of 33 or 39 per cent, depending upon the choice from the two calibration curves of Figure 10.

With the green filter, the two computed values would be 34 to 35 per cent.

Discussion of Method

The judgment of the extinction of a filament through a turbid medium depends upon the visual acuity of the observer, which varies considerably for different observers. It is therefore necessary with this instrument for each observer to obtain his own calibration curve. A moderately experienced observer can duplicate his calibration curve or rubber determinations within 1 per cent for observations repeated immediately or on succeeding days. However, it may be desirable for the observer to check his calibration occasionally to avoid errors arising from pronounced changes in his own visual acuity.

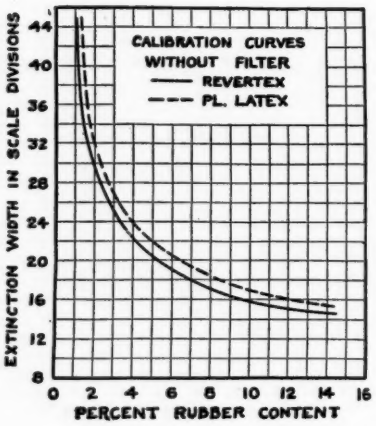


Figure 10

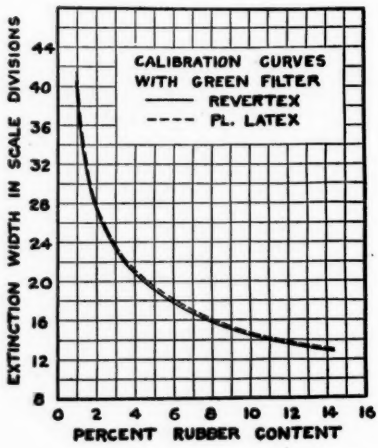


Figure 11

The effects of different visual acuities of observers may be diminished by using a photometric turbidimeter. The experimental microturbidimeter was modified to permit a photometric balance of the filament viewed through the extinction cell with an auxiliary filament viewed through a turbid filter. This was accomplished by inserting a piece of plate glass inclined 45 degrees to the axis of the microscope, between the color filter and the extinction cell of Figure 1. The auxiliary filament was so placed that this inclined glass plate superimposed the image of the auxiliary filament upon the image of the extinction filament. The procedure consisted of shifting the extinction cell until a photometric balance was obtained between the two filaments partially extinct by the extinction cell or the turbid filter. Curves plotted between the depths for photometric balance

and the rubber content of the diluted latex were similar in character to the extinction curves of Figure 5. This photometric type of turbidimeter is very susceptible to changes in intensity of either or both filaments. The microturbidimeter is much less susceptible to changes in intensity of the filament for latex measurements. An increase in the voltage on the 3.8-volt extinction light from 1.5 to 3.0 volts produced only a slight change in the extinction readings for latex. This change was due probably more to a change in the effective color of the filament than to a change in its intensity.

The judgment of extinction by an observer depends greatly upon the light history of his eye with respect to the intensity of light entering his eye just before making an observation. Since the extinction of the filament occurs at low light intensities, it is desirable for the observer's eye to be fully "dark adapted." Observations by a partially "light adapted" eye yield erratic results. Since the interval of "dark adaption" is considerable, the microturbidimeter should be used in a dark room or a room of low constant intensity of illumination.

The microturbidimeter with a green light filter permits the determination of the rubber content of latex with a probable precision of less than 1 per cent rubber content in 35 per cent latex. The time required for this determination is less than 5 minutes as compared with 2 or more hours for the long method involving coagulation, creping, and drying, or a probable half hour for the short method of coagulation and creping without drying. The precision is not so good as the long coagulation method, but is better than the short coagulation method.

Literature Cited

(1) Conklin, O. E., *J. Optical Soc. Am.*, **10**, 573 (1925).
(2) Tolman, R. C., and Vleit, E. B., *J. Am. Chem. Soc.*, **41**, 297 (1919).
(3) Wells, P. V., *Chem. Reviews*, **3**, 331 (1927).
(4) Whitby, G. S., "Plantation Problems of the Next Decade," paper presented before the Batavia Congress, 1914.

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